

ORGANIC ELECTROLUMINESCENCE ELEMENT

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Abstract of JP6207169

PURPOSE: To provide an organic electroluinescence element containing a specific quinoxaline compound, having high luminance, high luminous efficiency and long life and useful for electronic device, display element, etc.

CONSTITUTION: The element contains a quinoxaline compound of formula I (Z is single bond, O, etc.; X and Y are 1-6C alkyl, 6-18C aryl, etc.; n is 1-3) (e.g. 2,2',3,3'-tetraphenyl-6,6'-diquinoxaline). The compound of formula 1 is preferably used as a light-emitting layer or electron injection layer of an organic electroluminescence element. The compound of formula I can be produced e.g. by reacting an alpha-diketone of formula II with an o-phenylenediamine of formula III in a solvent such as chloroform under stirring for 0.1-20hr.

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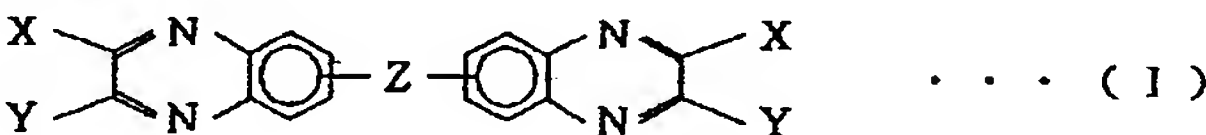
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(54) 【発明の名称】 有機エレクトロルミネッセンス素子

(57) 【要約】

【目的】 高輝度，高発光効率及び長寿命化を達成した有機エレクトロルミネッセンス素子の開発。

【構成】 一般式 (I)
【化 1 】

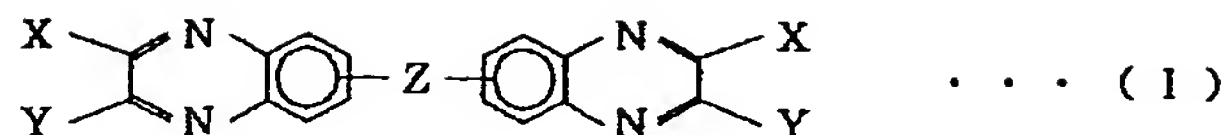


(式中の記号は明細書に記載の通りである。) で表されるキノキサリン化合物を含有する有機エレクトロルミネッセンス素子。

【特許請求の範囲】

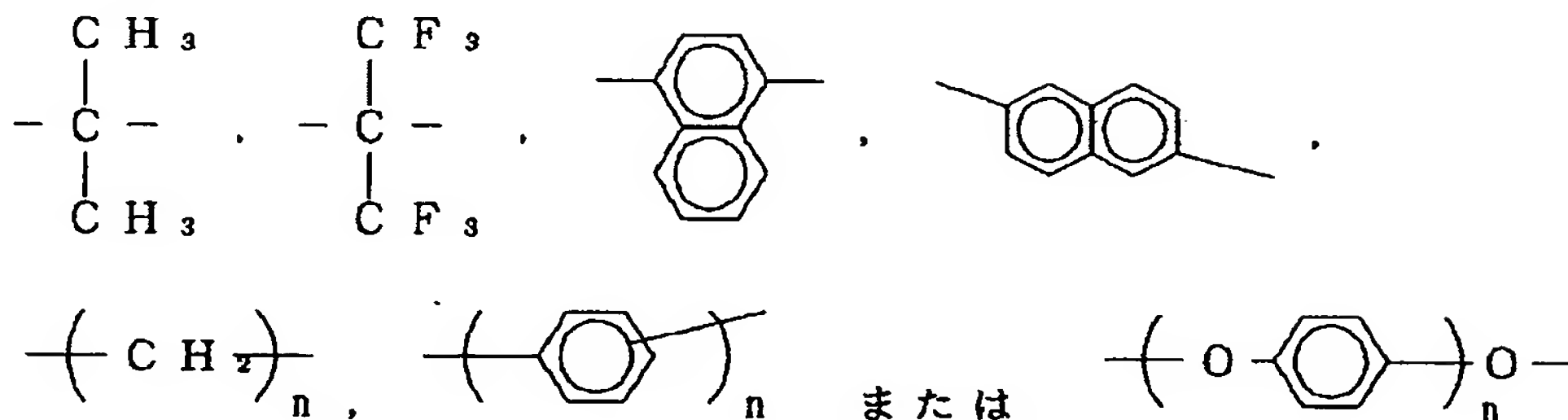
【化1】

【請求項1】 一般式(1)



(式中、Zは単結合、 $-\text{O}-$ 、 $-\text{SO}_2-$ 、 $-\text{S}-$ 、 $-\text{CH}=\text{CH}-$ 、 $-\text{CO}-$ 、 $-\text{NH}-$ 、 $-\text{N}=\text{N}-$ 、

【化2】



を示し、XおよびYはそれぞれ水素、炭素数1~6のアルキル基、置換または無置換の炭素数6~18のアリール基、あるいは置換または無置換の炭素数3~12の複素環残基を示す。上記置換基は、ニトロ基、アミノ基、シアノ基、水酸基、カルボキシ基、メチルチオ基、エチルチオ基、ハロゲン、炭素数1~6のアルコキシ基、炭素数1~6のアルコキシカルボニル基、炭素数1~8のジアルキルアミノ基、炭素数2~12のジアルキレンオキシ基、炭素数1~6のアルキレンジオキシ基、炭素数1~6のアルキレンオキシ基あるいは炭素数1~6のアルキル基である。また、nは1~3の整数を示す。)で表されるキノキサリン化合物を含有する有機エレクトロルミネッセンス素子。

【請求項2】 請求項1記載のキノキサリン化合物を含む層を、一対の電極間に挟持してなる有機エレクトロルミネッセンス素子。

【請求項3】 電子注入層の少なくとも一層が、請求項1記載のキノキサリン化合物を含有することを特徴とする有機エレクトロルミネッセンス素子。

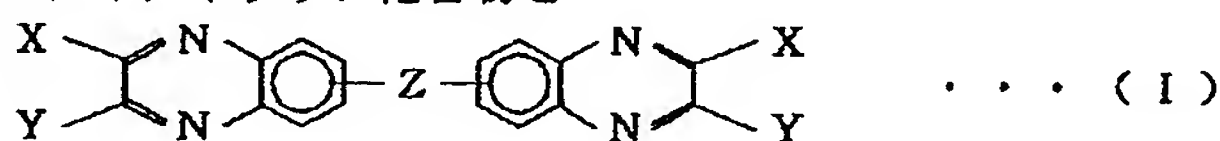
【請求項4】 発光層の少なくとも一層が、請求項1記載のキノキサリン化合物を含有することを特徴とする有機エレクトロルミネッセンス素子。

【請求項5】 正孔注入層の少なくとも一層が、請求項1記載のキノキサリン化合物を含有することを特徴とする有機エレクトロルミネッセンス素子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、有機エレクトロルミネッセンス素子に関し、詳しくは、キノキサリン化合物を



【0006】 (式中、Zは単結合、 $-\text{O}-$ 、 $-\text{SO}_2-$ 、 $-\text{S}-$ 、 $-\text{CH}=\text{CH}-$ 、 $-\text{CO}-$ 、 $-\text{NH}-$ 、 $-\text{N}=\text{N}-$ 、

有機エレクトロルミネッセンス素子の構成成分として用いることにより、高輝度、高発光効率及び長寿命化を達成した有機エレクトロルミネッセンス素子に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】 従来、有機エレクトロルミネッセンス素子(以下、有機EL素子と記す。)に電子注入層を設けて発光効率を高める試みがなされてきた。この場合、エキサイプレックスの形成が見られたり、高輝度の発光は得られるものの発光寿命が短いという欠点があった。また、長時間の通電により金属電極と有機層の剥離が発生したり、有機層と電極が結晶化し白濁化し発光輝度が低下するため、このような現象を防ぐ必要があった。キノキサリン化合物を有機EL素子の構成成分として用いた例として、米国特許第5077142号(1991年)で開示された2,3-ジフェニルキノキサリンがある。しかし、融点が124~125℃と低いため、有機EL素子のアモルファス薄膜層として用いても結晶化がすぐ起こり、殆ど発光しないという問題があった。そこで、本発明者らは、上記問題を解決すべく鋭意研究を重ねた。

【0003】

【課題を解決するための手段】 その結果、特定のキノキサリン化合物を有機EL素子の構成成分として用いることにより、上記問題点を解決できることを見出した。本発明は、かかる知見に基づいて完成したものである。

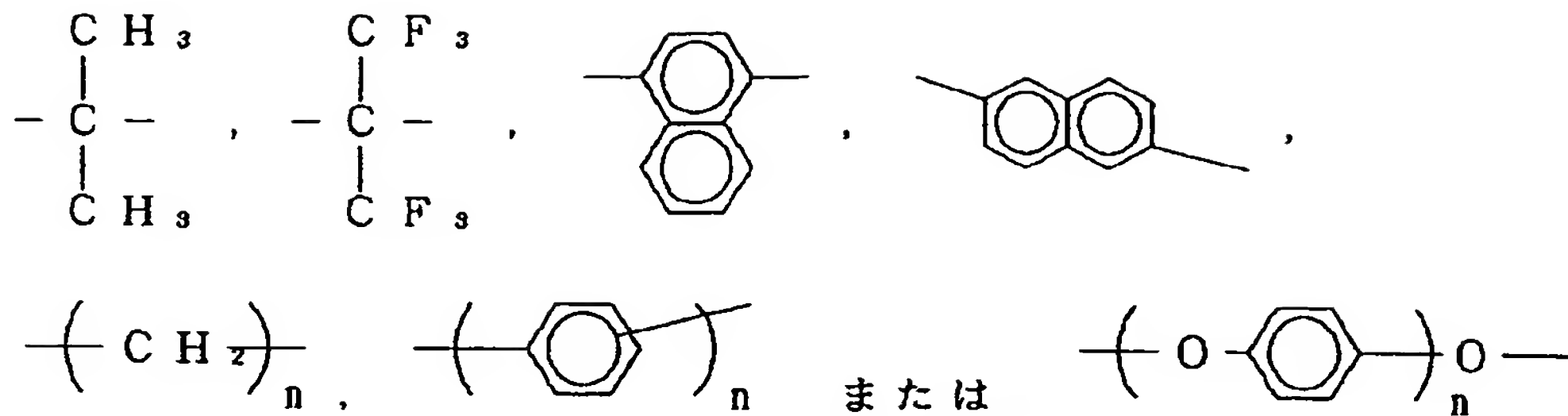
【0004】 すなわち、本発明は、一般式(1)

【0005】

【化3】

【0007】

【化4】



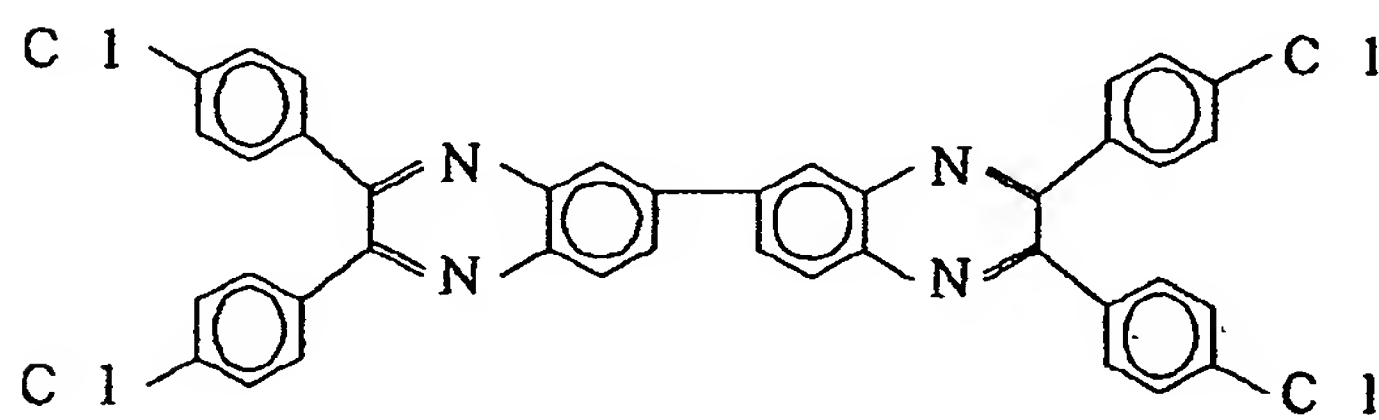
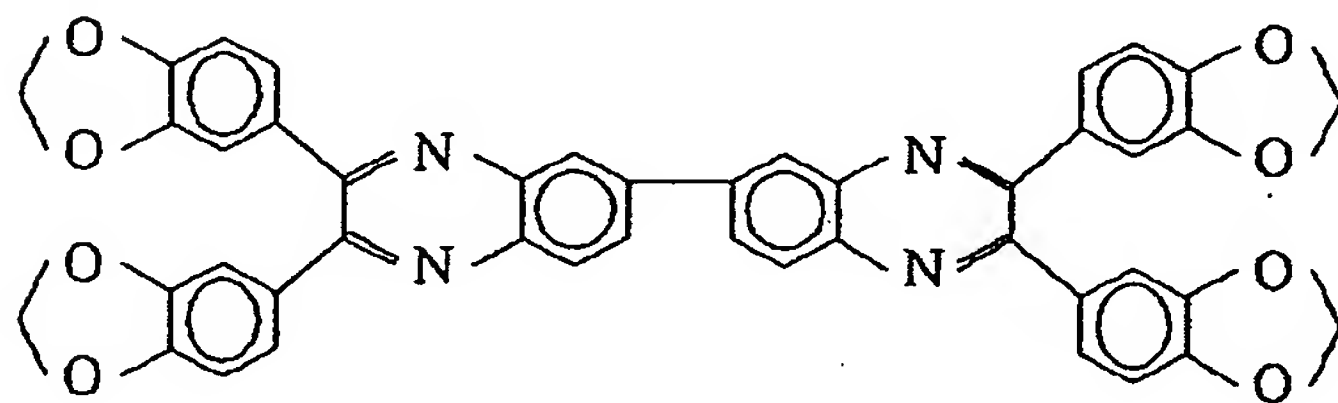
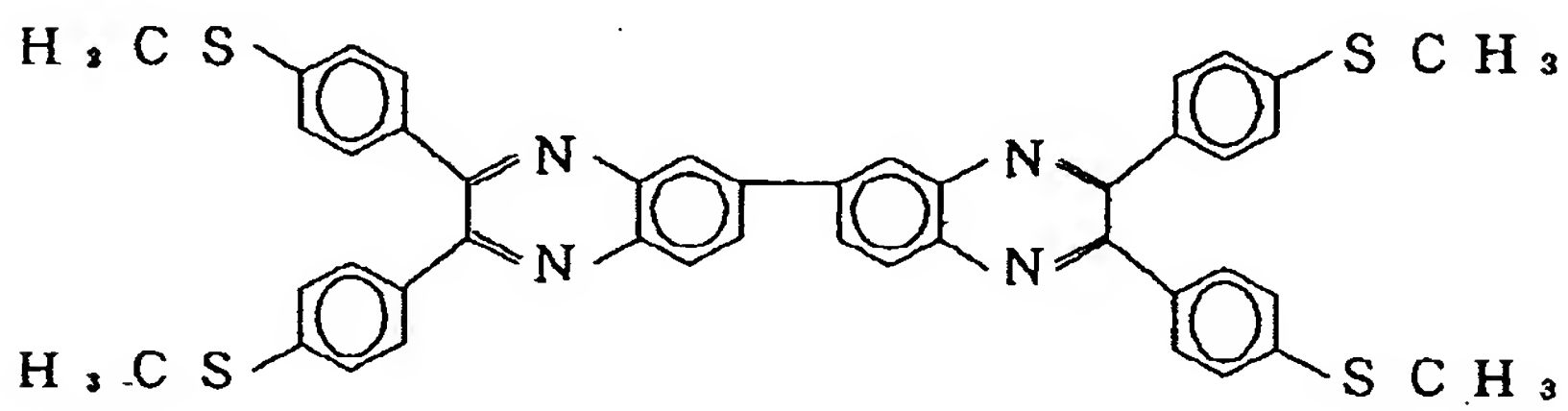
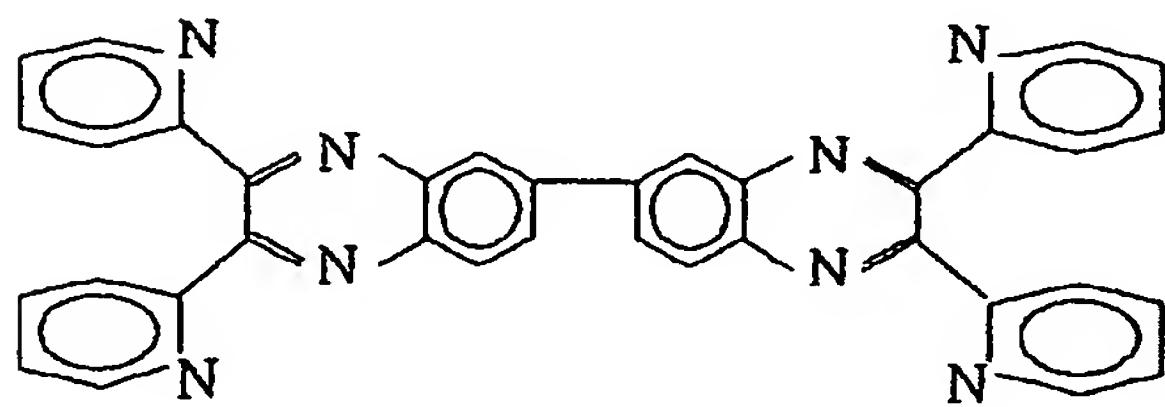
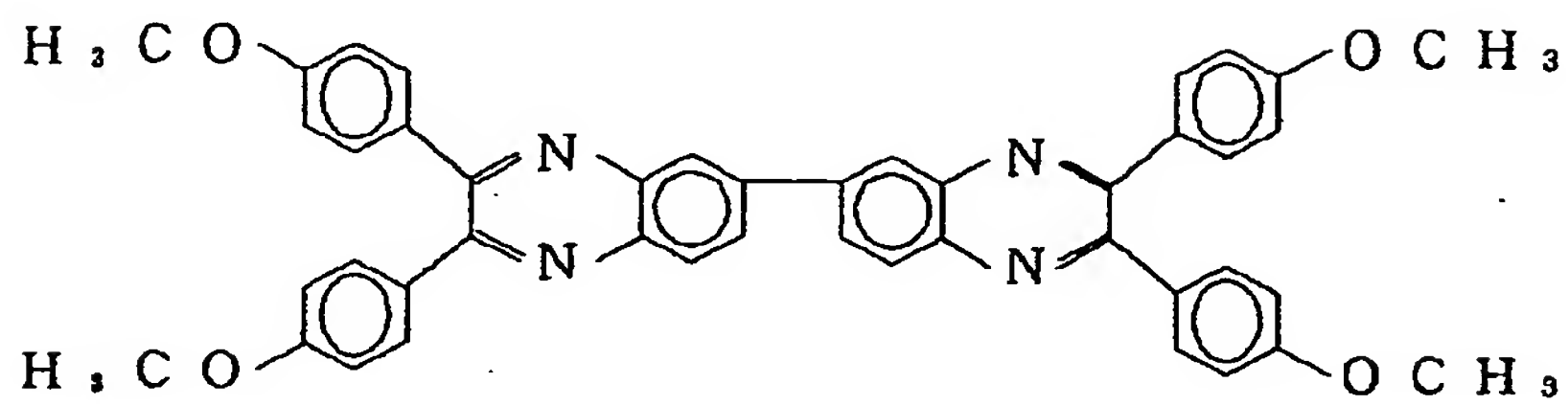
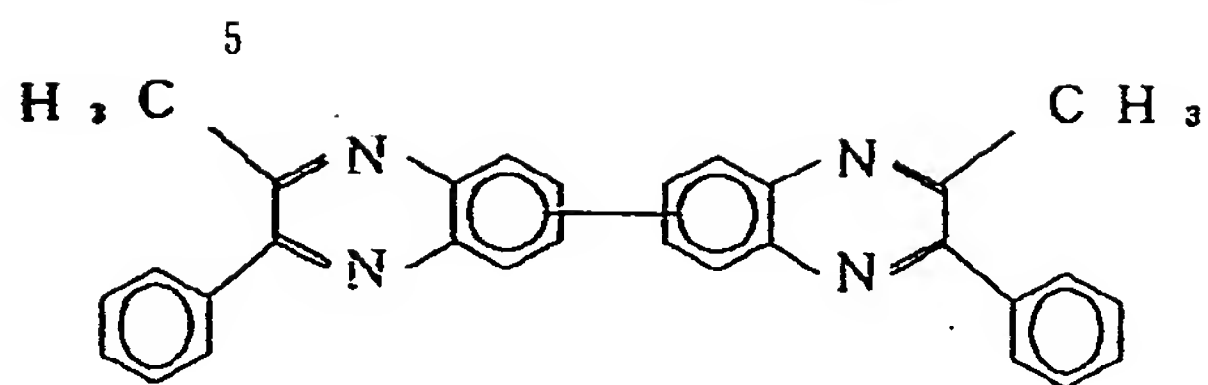
【0008】を示し、XおよびYはそれぞれ水素、炭素数1～6のアルキル基、置換または無置換の炭素数6～18のアリール基、あるいは置換または無置換の炭素数3～12の複素環残基を示す。上記置換基は、ニトロ基、アミノ基、シアノ基、水酸基、カルボキシ基、メチルチオ基、エチルチオ基、ハロゲン、炭素数1～6のアルコキシ基、炭素数1～6のアルコキシカルボニル基、炭素数1～8のジアルキルアミノ基、炭素数2～12のジアルキレンオキシ基、炭素数1～6のアルキレンジオキシ基、炭素数1～6のアルキレンオキシ基あるいは炭素数1～6のアルキル基である。また、nは1～3の整数を示す。)で表されるキノキサリン化合物を含有する有機エレクトロルミネッセンス素子を提供するものである。

【0009】本発明は、上記一般式(I)で表されるキノキサリン化合物を含有した有機EL素子である。ここで、一般式(I)のXおよびYとしては、水素、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、イソブチル基、tert-ブチル基、sec-ブチル基、イソペンチル基、tert-ペンチル基、ネオペンチル基、ヘキシル基、イソヘキシル基、シクロヘキシル基などの炭素数1～6のアルキル基、置換または無置換のフェニル基、ビフェニル基、ナフチル基、アントリル基、ターフェニル基、ピレニル基などの炭素数6～18のアリール基、置換または無置換のフラン基、チオフェン基、ピロール基、ピラゾール基、イミダゾール基、トリアゾール基、イソオキサゾール基、オキサゾール基、フラザン基、イソチアゾール基、チアゾール基、ピリジン基、ピリミジン基、ピラジン基、オキサジン基、チアジン基、ベンゾフラン基、チオナフテン基、ベンゾオキサゾール基、ベンゾチアゾール基、キノリン基、イソキノリン基、キノキサリン基、キナゾリン基、フタラジン基、アクリジン基、フェナジン基、チアントレン基などの炭素数3～12の複素環残基を示す。この複素環残基のうち、XおよびYの少なくとも一方がヘテロ原子(N, S, O)を含むものであることが好ましい。上記置換基としては、ニトロ基、アミノ基、シアノ

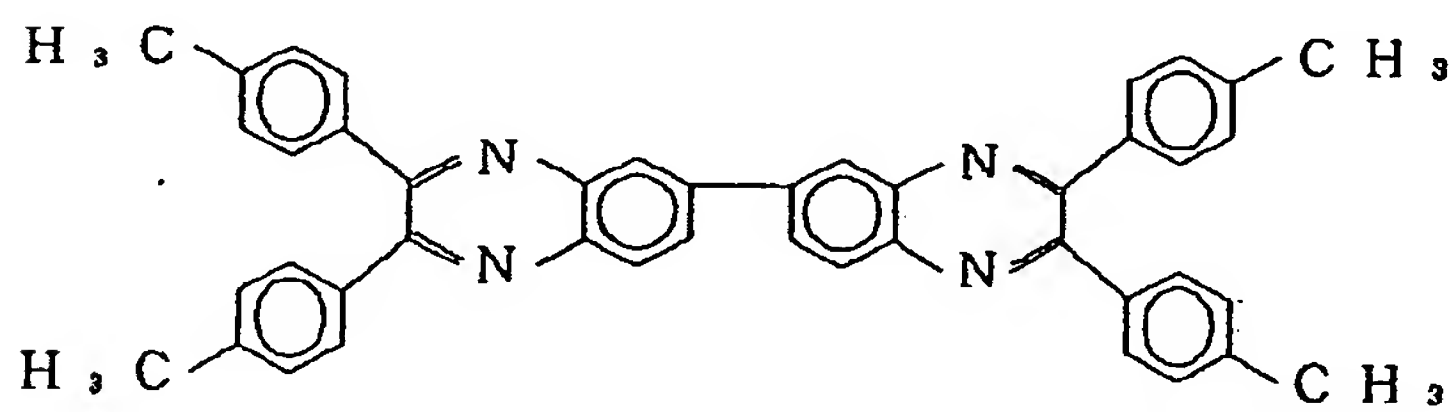
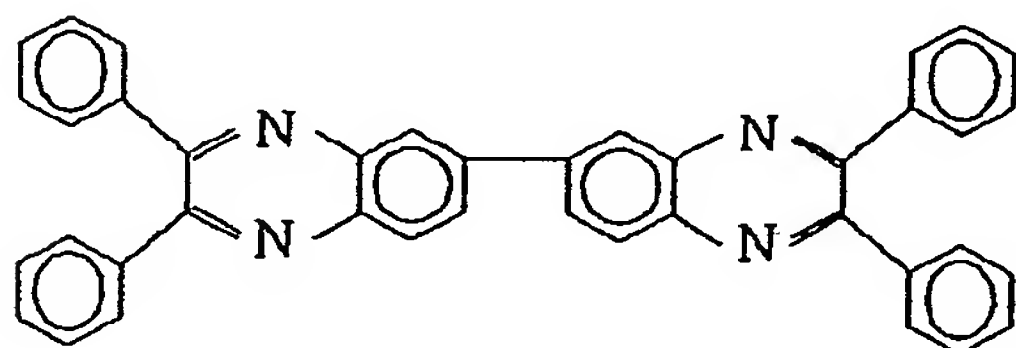
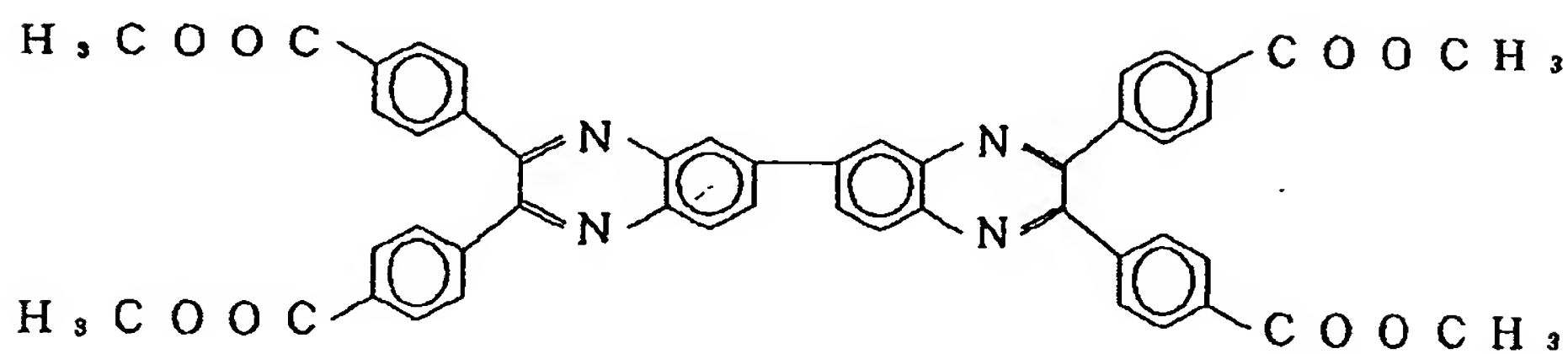
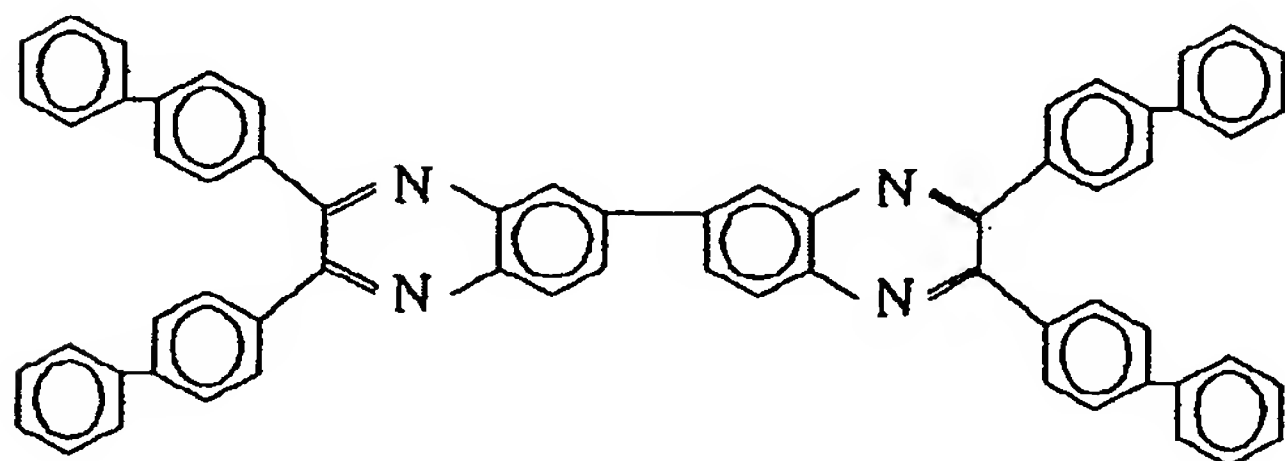
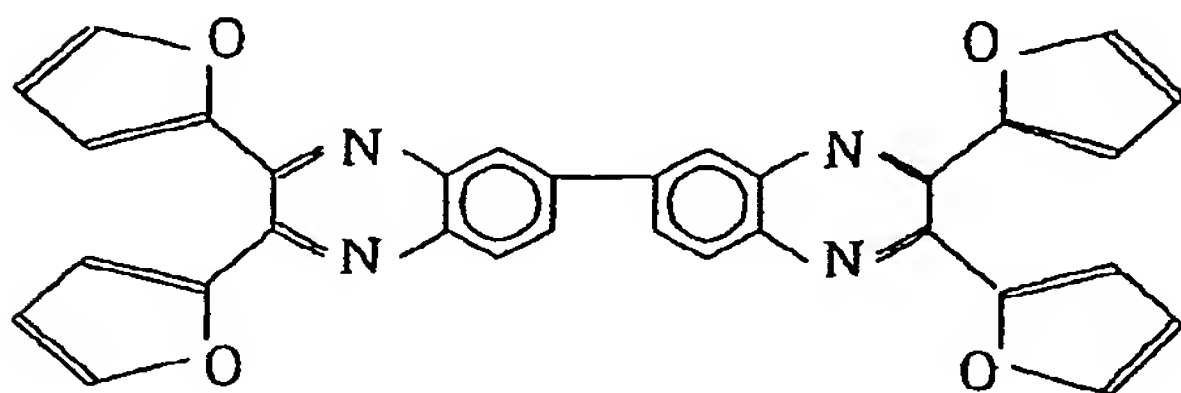
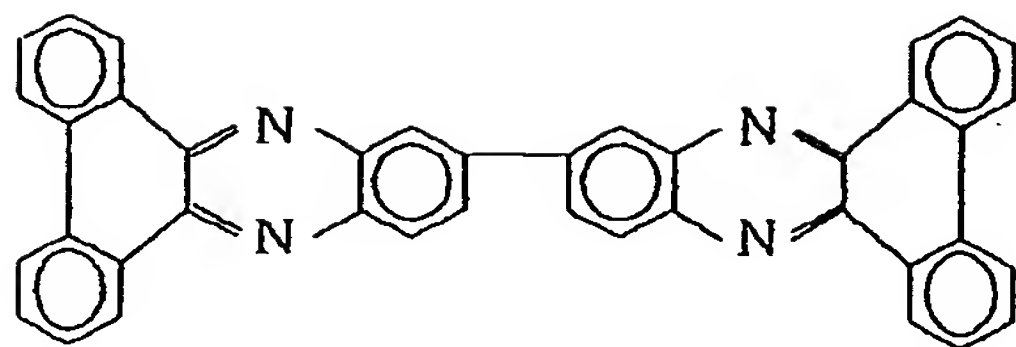
基、水酸基、カルボキシ基、メチルチオ基、エチルチオ基、ハロゲン(フッ素、塩素、臭素、碘素)、メトキシ基、エトキシ基、プロポキシ基、イソプロポキシ基、n-ブトキシ基、イソブトキシ基、tert-ブトキシ基、sec-ブトキシ基、イソペントキシ基、tert-ペントキシ基、ネオペントキシ基、ヘキシルオキシ基、イソヘキシルオキシ基などの炭素数1～6のアルコキシ基、フェノキシカルボニル基、メトキシカルボニル基、エトキシカルボニル基、プロポキシカルボニル基、tert-ブトキシカルボニル基などの炭素数1～6のアルコキシカルボニル基、ジメチルアミノ基、ジエチルアミノ基、ジプロピルアミノ基、ジイソプロピルアミノ基、ジ(n-ブチル)アミノ基、ジイソブチルアミノ基、ジ(tert-ブチル)アミノ基、ジ(sec-ブチル)アミノ基などの炭素数1～8のジアルキルアミノ基、ジメチレンオキシ基、ジエチレンオキシ基、ジプロピレンオキシ基などの炭素数2～12のジアルキレンオキシ基、メチレンジオキシ基、エチレンジオキシ基、プロピレンジオキシ基などの炭素数1～6のアルキレンジオキシ基、メチレンオキシ基、エチレンオキシ基、プロピレンオキシ基などの炭素数1～6のアルキレンオキシ基、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、イソブチル基、tert-ブチル基、sec-ブチル基、イソペンチル基、tert-ペンチル基、ネオペンチル基、ヘキシル基、イソヘキシル基などの炭素数1～6のアルキル基などが挙げられる。上記XとYは、置換基間で結合して飽和または不飽和の4～7員環を形成してもよい。さらに、本発明で用いるキノキサリン化合物は、XとYが異なる場合、キノキサリン環の6位と7位の結合位置により6, 6'-一体、6, 7'-一体、7, 7'-一体の構造異性体を生じるが、単独の異性体でもそれら異性体の混合物でもよい。本発明で用いられる上記一般式(I)で表されるキノキサリン化合物としては、

【0010】

【化5】

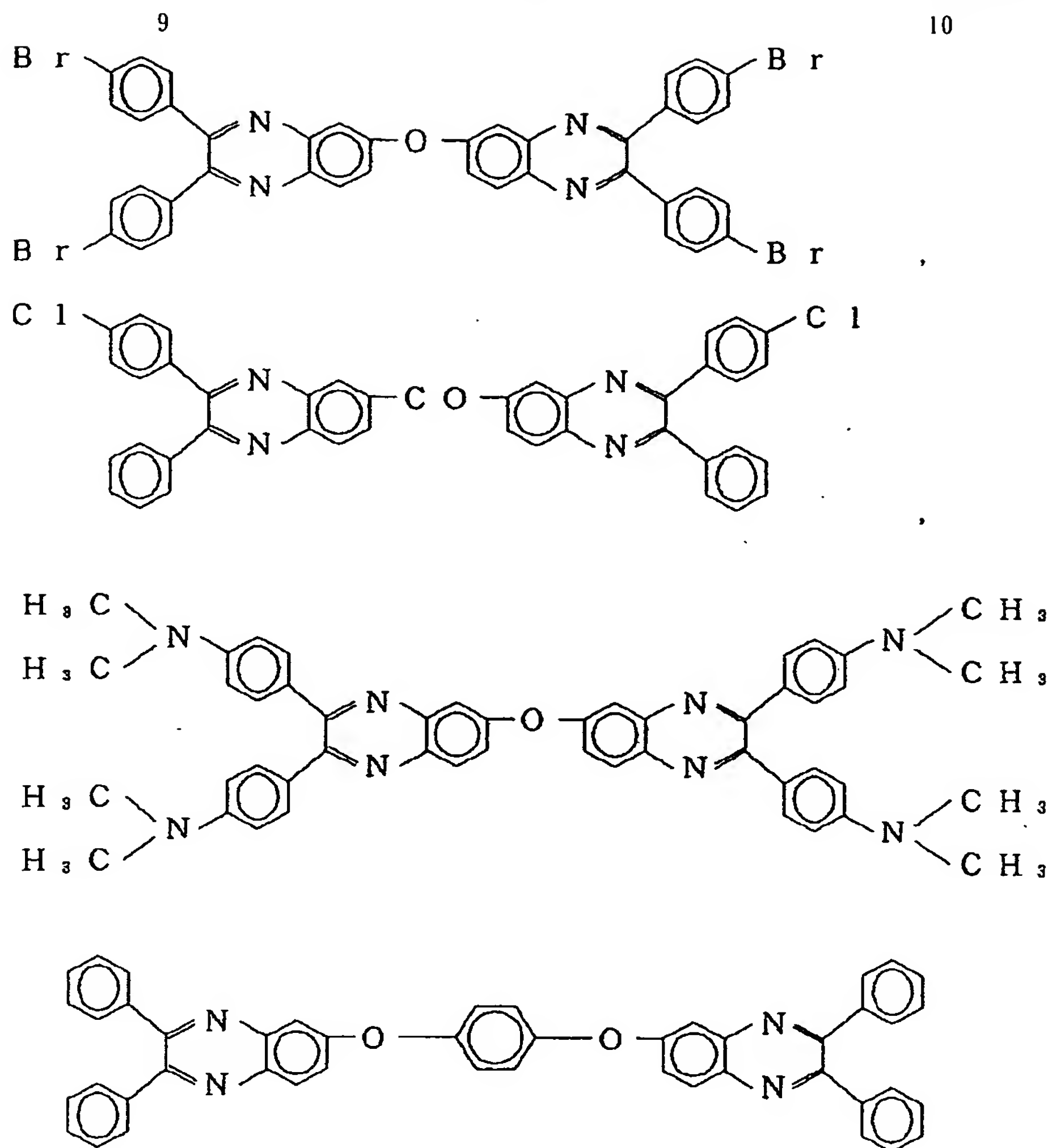


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【 0 0 1 2 】

40 【 化 7 】



【0013】などが挙げられる。本発明は、上記一般式 (I) で表される構造を有するキノキサリン化合物を含有する有機EL素子であり、その素子構成としては、例えば陽極／正孔注入層／発光層／電子注入層／陰極、陽極／発光層／電子注入層／陰極、陽極／正孔注入層／発光層／陰極、陽極／発光層／陰極型などが挙げられる。上記一般式 (I) で表される構造を有するキノキサリン化合物は、好ましくは発光層、電子注入層を構成するものである。素子構成においては、正孔注入層や電子注入層は必要ではないが、これらの層を有する素子は発光性能が向上する利点がある。また、一对の電極間に上記正孔注入層、発光層、電子注入層を混合させた形で挟持させてもよい。さらに、各成分を安定に存在させるため、高分子化合物などのバインダーを用いて混合層を作製してもよい。

【0014】ここで、本発明の有機EL素子として、陽極／正孔注入層／発光層／電子注入層／陰極型を例にして説明する。本発明の素子は、基板に支持されていることが好ましい。この基板については特に制限はなく、従来の有機EL素子に慣用されているものであればよく、例えばガラス、透明プラスチック、石英などからなるも

のを用いることができる。

【0015】このEL素子における正極としては、仕事関数の大きい (4 eV以上) 金属、合金、電気伝導性化合物及びこれらの混合物を電極物質とするものが好ましく用いられる。このような電極物質の具体例としてはAuなどの金属、CuI、ITO、SnO₂、ZnOなどの導電性透明材料が挙げられる。該正極は、これらの電極物質を蒸着やスパッタリングなどの方法により、薄膜を形成させることにより作製することができる。この電極より発光を取り出す場合には、透過率を10%より大きくすることが望ましく、また、電極としてのシート抵抗は数百Ω/□以下が好ましい。さらに膜厚は材料にもよるが、通常10nm~1μm、好ましくは10~200nmの範囲で選ばれる。

【0016】一方、陰極としては、仕事関数の小さい (4 eV以下) 金属、合金、電気伝導性化合物及びこれらの混合物を電極物質とするものが用いられる。このような電極物質の具体例としては、ナトリウム、ナトリウム-カリウム合金、マグネシウム、リチウム、マグネシウム/銅混合物、マグネシウム/銀混合物、Al/Al₂O₃、インジウムなどが挙げられる。該陰極は、これ

らの電極物質を蒸着やスパッタリングなどの方法により、薄膜を形成させることにより、作製することができる。また、電極としてのシート抵抗は数百 Ω/\square 以下が好ましく、膜厚は通常10~500nm、好ましくは50~200nmの範囲で選ばれる。なお、発光を透過させるため、有機EL素子の陽極又は陰極のいずれか一方が、透明又は半透明であれば発光効率が向上し好都合である。

【0017】本発明の発光層の発光材料としては、上記一般式(I)で表される構造を有するキノキサリン化合物が好ましい。このキノキサリン化合物が発光層以外で用いられている場合は、発光層の発光材料について特に制限されることはなく、従来公知の化合物の中から任意のものを選択して用いることができる。

【0018】上記キノキサリン化合物以外の発光材料としては、例えば、多環縮合芳香族化合物、ベンゾオキサゾール系、ベンゾチアゾール系、ベンゾイミダゾール系などの蛍光増白剤、金属キレート化オキサノイド化合物、ジスチリルベンゼン系化合物など薄膜形成性の良い化合物を用いることができる。ここで、上記多環縮合芳香族化合物としては、例えばアントラセン、ナフタレン、フェナントレン、ピレン、クリセン、ペリレン骨格を含む縮合環発光物質等を挙げることができる。

【0019】上記ベンゾオキサゾール系、ベンゾチアゾール系、ベンゾイミダゾール系などの蛍光増白剤としては、例えば特開昭59-194393号公報に記載されているものを用いることができ、その代表例としては、2, 5-ビス(5, 7-ジ-*t*-ペンチル-2-ベンゾオキサゾリル)-1, 3, 4-チアジアゾール; 4, 4'-ビス(5, 7-*t*-ペンチル-2-ベンゾオキサゾリル)スチルベン; 4, 4'-ビス(5, 7-ジ-(2-メチル-2-ブチル)-2-ベンゾオキサゾリル)スチルベン; 2, 5-ビス(5, 7-ジ-*t*-ペンチル-2-ベンゾオキサゾリル)チオフエン; 2, 5-ビス(5-(α , α , -ジメチルベンジル)-2-ベンゾオキサゾリル)チオフエン; 2, 5-ビス(5, 7-ジ-(2-メチル-2-ブチル)-2-ベンゾオキサゾリル)-3, 4-ジフェニルチオフエン; 2, 5-ビス(5-メチル-2-ベンゾオキサゾリル)チオフエン; 4, 4'-ビス(2-ベンゾオキサゾリル)ビフェニル; 5-メチル-2-(2-(4-(5-メチル-2-ベンゾオキサゾリル)フェニル)ビニル)ベンゾオキサゾール; 2-(2-(4-クロロフェニル)ビニル)ナフト(1, 2-d)オキサゾールなどのベンゾオキサゾール系、2, 2'-(*p*-フェニレンジビニレン)-ビスベンゾチアゾールなどのベンゾチアゾール系、2-(2-(4-(2-ベンゾイミダゾリル)フェニル)ビニル)ベンゾイミダゾール; 2-(2-(4-カルボキシフェニル)ビニル)ベンゾイミダゾールなどのベンゾイミダゾール系などの蛍光増白剤が挙げられる。

【0020】上記金属キレート化オキサノイド化合物としては、例えば特開昭63-295695号公報に記載されているものを用いることができる。その代表例としては、トリス(8-キノリノール)アルミニウム、ビス(8-キノリノール)マグネシウム、ビス(ベンゾ(f)-8-キノリノール)亜鉛、ビス(2-メチル-8-キノリノール)アルミニウムオキシド、トリス(8-キノリノール)インジウム、トリス(5-メチル-8-キノリノール)アルミニウム、8-キノリノールリチウム、トリス(5-クロロ-8-キノリノール)ガリウム、ビス(5-クロロ-8-キノリノール)カルシウム、ポリ(亜鉛(II)-ビス(8-ヒドロキシ-5-キノリノニル)メタン)などの8-ヒドロキシキノリン系金属鎖体やジリチウムエピンドリジオンなどが挙げられる。

【0021】他には、欧州特許第0373582号明細書に記載のジスチリルベンゼン誘導体、同0388768号明細書に記載のジメチリデン誘導体、特開平2-191694号公報のクマリン誘導体、特開平2-252793号公報のジスチリルピラジン誘導体、特開平2-196885号公報のペリレン誘導体、特開平2-255789号公報のナフタレン誘導体、特開平2-289676号公報及び同2-88689号公報のフタロペリノン誘導体、特開平2-250292号公報のスチリルアミン誘導体及び同2-289675号公報のシクロペンタジエン誘導体など、目的とする発光色及び性能などから適宜選択することができる。上記の有機化合物からなる発光層は、所望に応じて2層以上の積層構造でもよく、米国特許第4, 769, 292号明細書に開示されているように蛍光物質を加えて形成してもよい。この場合上記有機化合物は薄膜状の層であり、発光領域の機能の注入機能及び発光機能の一部を受持ち、一方、蛍光物質はその有機化合物の層の中に微量(数モル%以下)存在させ、電子と正孔の再結合に応答して発光するといった発光機能の一部を担っている。さらに、発光領域に用いる有機化合物は薄膜性を有していない化合物であってもよく、このような化合物の例としては、1, 4-ジフェニル-1, 3-ブタジエン; 1, 1, 4, 4-テトラフェニル-1, 3-ブタジエン; テトラフェニルシクロペンタジエンなどが挙げられる。しかし、これらの薄膜性を有しない材料は、素子の寿命が短い欠点を有する。この発光層は、これらの発光材料一種又は二種以上からなる一層で構成されてもよいし、あるいは、前記発光層とは別種の化合物からなる発光層を積層したものであってもよい。

【0022】次に、本発明の有機EL素子の正孔注入層は、正孔伝達化合物から成るものであって、陽極より注入された正孔を発光層に伝達する機能を有し、この正孔注入層を陽極と発光層の間に介在させることにより、より低い電界で多くの正孔が発光層に注入され、そのう

え、発光層に陰極又は電子注入層より注入された電子は、発光層と正孔注入層の界面に存在する電子の障壁により、発光層内の界面に累積され発光効率が向上するなど発光性能の優れた素子となる。このような正孔注入層に用いられる正孔伝達化合物は、電界を与えられた2個の電極間に配置されて陽極から正孔が注入された場合、正孔を適切に発光層へ伝達しうるものであり、例えば $10^4 - 10^6 \text{ V/cm}$ の電界印加時に少なくとも $10^{-6} \text{ cm}^2 / \text{V} \cdot \text{秒}$ の正孔移動度を有するものが好適である。この正孔伝達化合物については、前記の好ましい性質を有するものであれば特に制限はなく、従来、光導伝材料において、正孔の電荷注入輸送材料として慣用されているものやEL素子の正孔注入層に使用される公知のものの中から任意のものを選択して用いることができる。

【0023】上記正孔伝達化合物としては、例えば前記一般式(I)で表されるキノキサリン化合物、トリアゾール誘導体、オキサジアゾール誘導体(米国特許第3,189,447号などに記載のもの)、イミダゾール誘導体、ポリアリールアルカン誘導体、ピラゾリン誘導体及びピラゾロン誘導体、フェニレンジアミン誘導体、アリールアミン誘導体、アミノ置換カルコン誘導体、オキサゾール誘導体、スチリルアントラセン誘導体、フルオレノン誘導体、ヒドラゾン誘導体、スチルベン誘導体などを挙げることができる。また、電荷注入輸送材料としては、シラザン誘導体、ポリシラン系、アニリン系共重合体、また、導電性高分子オリゴマー、特にチオフェンオリゴマーなどが挙げられる。

【0024】本発明においては、上記の正孔伝達化合物または電荷注入輸送材料を正孔注入材料として使用することができるが、次に示すポルフィリン化合物(特開昭63-2956965号公報などに記載のもの)及び芳香族第三級アミン化合物及びスチリルアミン化合物(米国特許第4,127,412号明細書、特開昭53-27033号公報、同54-58445号公報、同54-149634号公報、同54-64299号公報、同55-79450号公報、同55-144250号公報、同56-119132号公報、同61-295558号公報、同61-98353号公報、同63-295695号公報など参照)、特に該芳香族第三級アミン化合物を用いることが好ましい。該ポルフィリン化合物の代表例としては、ポルフィン、1,10,15,20-テトラフェニル-21H,23H-ポルフィン銅(II);1,10,15,20-テトラフェニル21H,23H-ポルフィン亜銅(II);5,10,15,20-テトラキス(ペンタフルオロフェニル)-21H,23H-ポルフィン;シリコンフタロシアニンオキシド;アルミニウムフタロシアニクロリド;フタロシアニン(無金属);ジリチウムフタロシアニン;銅テトラメチルフタロシアニン;銅フタロシアニン;クロムフタロシアニン;亜鉛フ

タロシアニン;鉛フタロシアニン;チタニウムフタロシアニンオキシド;マグネシウムフタロシアニン;銅オクタメチルフタロシアニンなどが挙げられる。

【0025】また、該芳香族第三級アミン化合物及びスチリルアミン化合物の代表例としては、N,N,N',N'-テトラフェニル-4,4'-ジアミノフェニル;N,N'-ジフェニル-N,N'-ジ(3-メチルフェニル)-4,4'-ジアミノビフェニル(TPDA);2,2-ビス(4-ジ-p-トリルアミノフェニル)プロパン;1,1-ビス(4-ジ-p-トリルアミノフェニル)シクロヘキサン;N,N,N',N'-テトラ-p-トリル-4,4'-ジアミノビフェニル;1,1-ビス(4-ジ-p-トリルアミノフェニル)-4-フェニルシクロヘキサン;ビス(4-ジメチルアミノ-2-メチルフェニル)フェニルメタン;ビス(4-ジ-p-トリルアミノフェニル)フェニルメタン;N,N'-ジフェニル-N,N'-ジ(4-メトキシフェニル)-4,4'-ジアミノビフェニル;N,N,N',N'-テトラフェニル-4,4'-ジアミノジフェニルエーテル;4,4'-ビス(ジフェニルアミノ)クオードリフェニル;N,N,N-トリ(p-トリル)アミン;4-(ジ-p-トリルアミノ)-4'-[4(ジ-p-トリルアミノ)スチリル]スチルベン;4-N,N-ジフェニルアミノ-(2-ジフェニルビニル)ベンゼン;3-メトキシ-4'-N,N-ジフェニルアミノスチルベンゼン;N-フェニルカルバゾールなどが挙げられる。また、Si, SiC, CdSなどの無機物半導体の結晶、非晶材料も用いることができる。この正孔注入層は、これらの正孔注入材料一種又は二種以上からなる一層で構成されてもよいし、あるいは、前記正孔注入層とは別種の化合物からなる正孔注入層を積層したものであってもよい。

【0026】また、本発明で用いる有機EL素子の電子注入層は、電子注入材料から成るものであって、陰極より注入された電子を発光層に伝達する機能を有している。本発明の場合は、上記一般式(I)で表される化合物が好ましい。このキノキサリン化合物が、電子注入層以外で用いられている場合は、電子注入材料について特に制限されることはなく、従来公知の化合物の中から任意のものを選択して用いることができる。

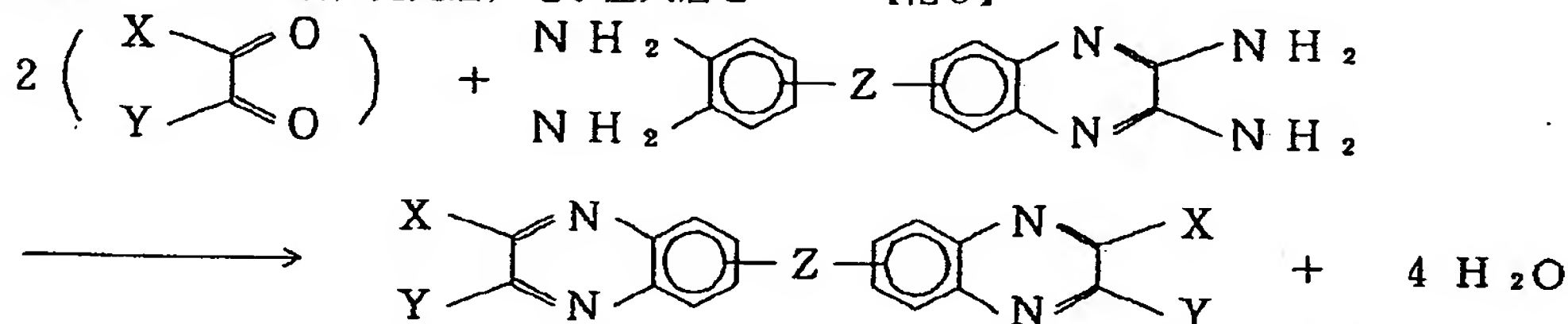
【0027】この電子注入層は、これらの電子注入材料1種又は2種以上からなる一層で構成されてもよいし、あるいは、前記層とは別種の化合物からなる電子注入層を積層したものであってもよい。さらに無機物であるp型-Si, p型-SiCによる正孔注入材料、n型 α -Si, n型 α -SiCによる電子注入材料を電子注入材料として用いることができる。例えば、国際公開WO90/05998に開示されている無機半導体などが挙げられる。

【0028】次に、本発明の方法において、有機EL素

子を作製する好適な例を説明する。例として、前記の陽極／正孔注入層／発光層／電子注入層／陰極からなるE L素子の作製法について説明すると、まず適当な基板上に、所望の電極物質、例えば陽極用物質からなる薄膜を、1 μm以下、好ましくは10～200 nmの範囲の膜厚になるように、蒸着やスパッタリングなどの方法により形成させ、陽極を作製する。次に、この上に素子材料である正孔注入層、発光層、電子注入層の材料からなる薄膜を形成させる。この薄膜化の方法としては、前記の如くスピコート法、キャスト法、蒸着法などがあるが、均質な膜が得られやすく、かつピンホールが生成しにくいなどの点から、真空蒸着法が好ましい。この薄膜化に、この蒸着法を採用する場合、その蒸着条件は、使用する化合物の種類、分子堆積膜の目的とする結晶構造、会合構造などにより異なるが、一般にボート加熱温度50～400℃、真空度 $10^{-6} \sim 10^{-3}$ Pa、蒸着速度0.01～50 nm/秒、基板温度-50～300℃、膜厚5 nm～5 μmの範囲で適宜選ぶことが望ましい。これらの層の形成後、その上に陰極用物質からなる薄膜を、1 μm以下好ましくは50～200 nmの範囲の膜

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【0032】具体的には、α-ジケトンおよびo-フェニレンジアミン誘導体をクロロホルム、アルコール（メタノール、エタノール、プロパノール、ブタノール、アミルアルコールなど）または酢酸などの溶媒中で攪拌または加熱攪拌するか、無溶媒のまま200℃前後で加熱攪拌する。この反応時間は0.1～20時間が好ましい。

混合させた形で挟持させた陽極／発光層／陰極からなる素子の作製方法としては、例えば適当な基板の上に、陽極用物質からなる薄膜を形成し、正孔注入材料、発光材料、電子注入材料、ポリビニルカルバゾール、ポリカーボネート、ポリアリレート、ポリエステル、ポリエーテルなどの結着剤などからなる溶液を塗布するか、又はこの溶液から浸漬塗工法により薄膜を形成させ発光層とし、その上に陰極用物質からなる薄膜を形成させるものがある。ここで、作製した発光層上に、さらに発光層または電子注入層の材料となる素子材料を真空蒸着し、その上に陰極用物質からなる薄膜を形成させてもよい。

【0029】このようにして得られたE L素子に、直流電圧を印加する場合には、陽極を＋、陰極を－の極性として電圧5～40 V程度を印加すると、発光が観測できる。また、逆の極性で電圧を印加しても電流は流れずに発光は全く生じない。さらに、交流電圧を印加する場合には、正極が＋、負極が－の状態になったときのみ発光する。なお、印加する交流の波形は任意でよい。

【0030】ここで、本発明の特徴である一般式（I）で表されるキノキサリン化合物の合成方法について簡単に触れておく。なお、本発明で用いるキノキサリン化合物の合成方法は、下記方法に限定されるものではない。一般式（I）のキノキサリン化合物の合成方法は、下記合成スキームによる。

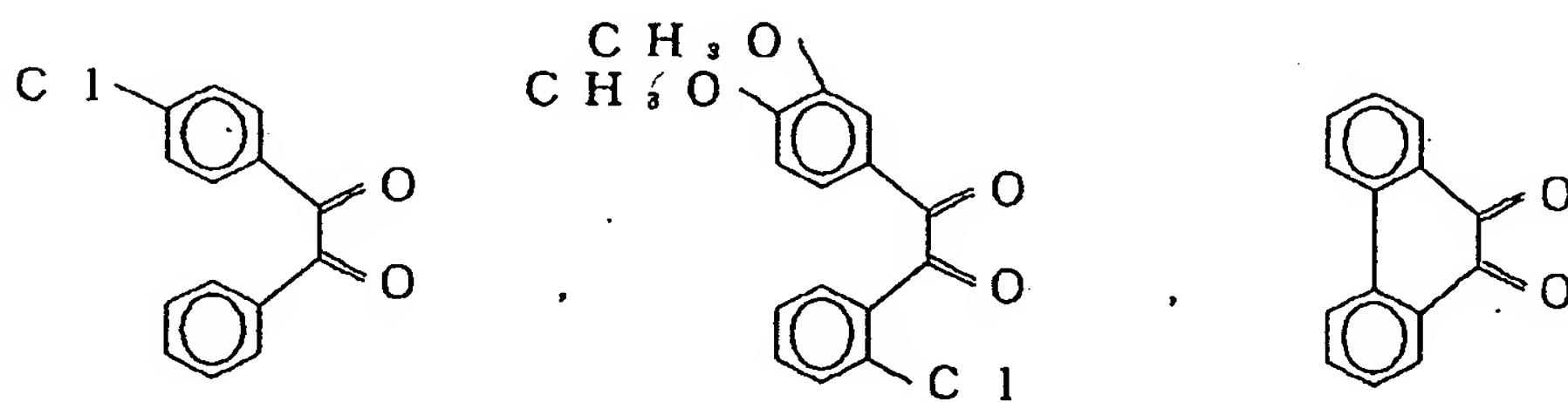
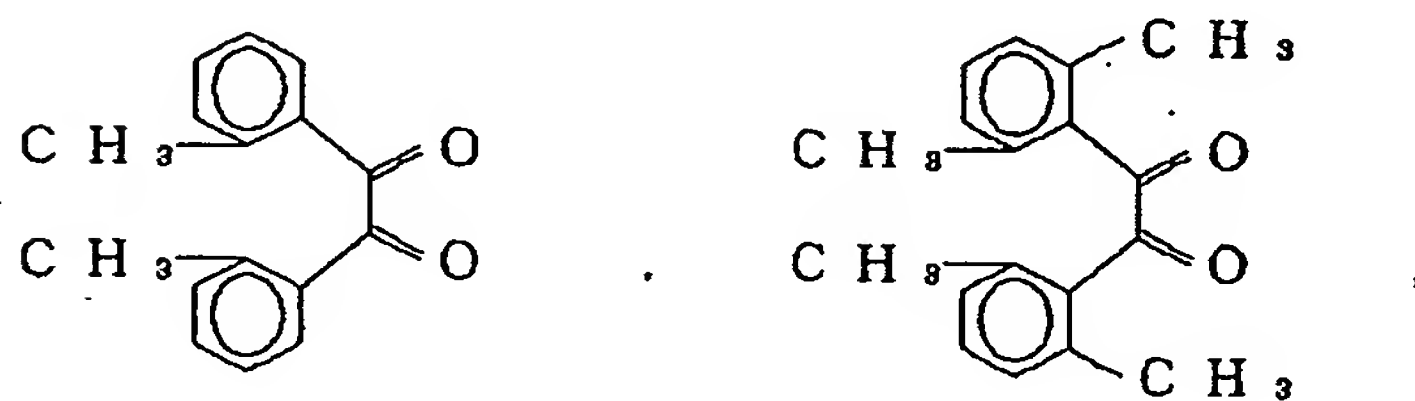
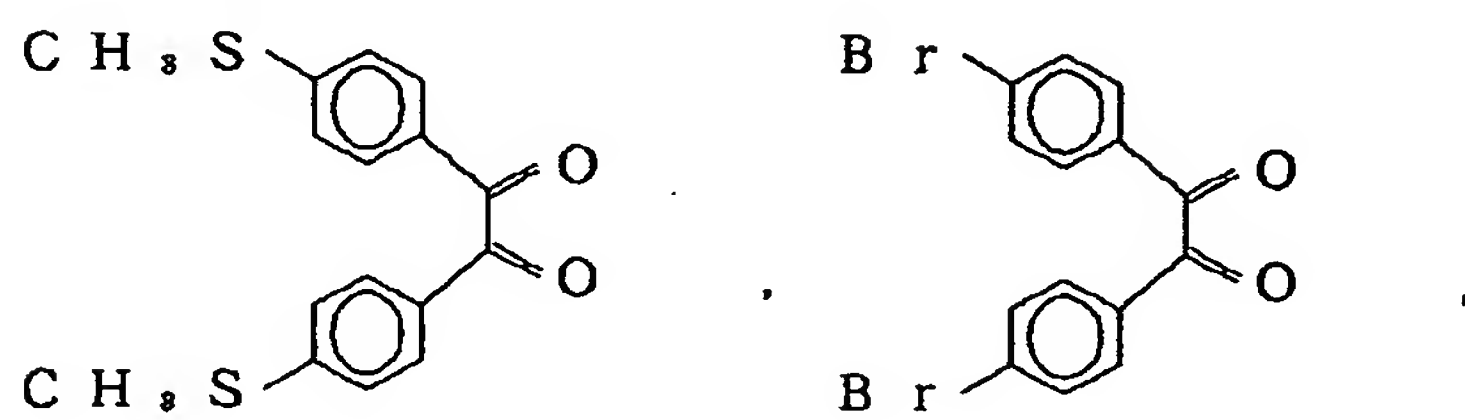
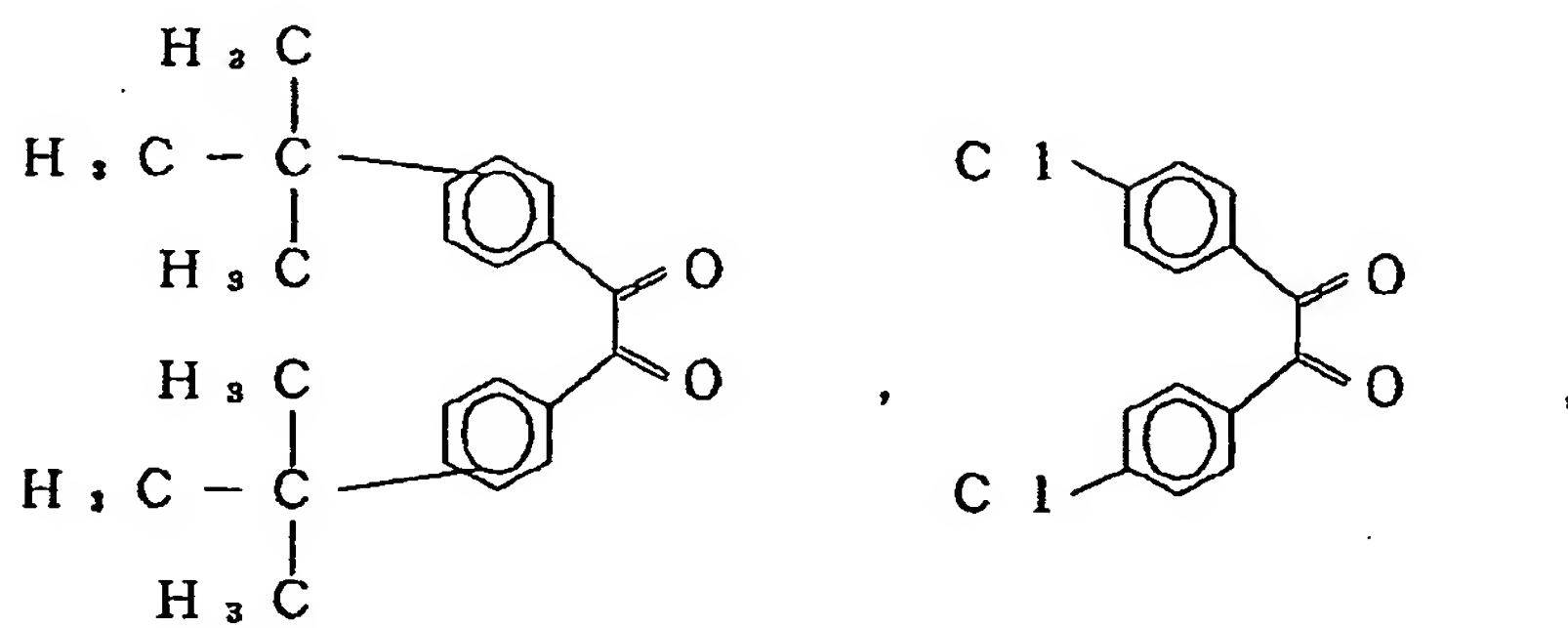
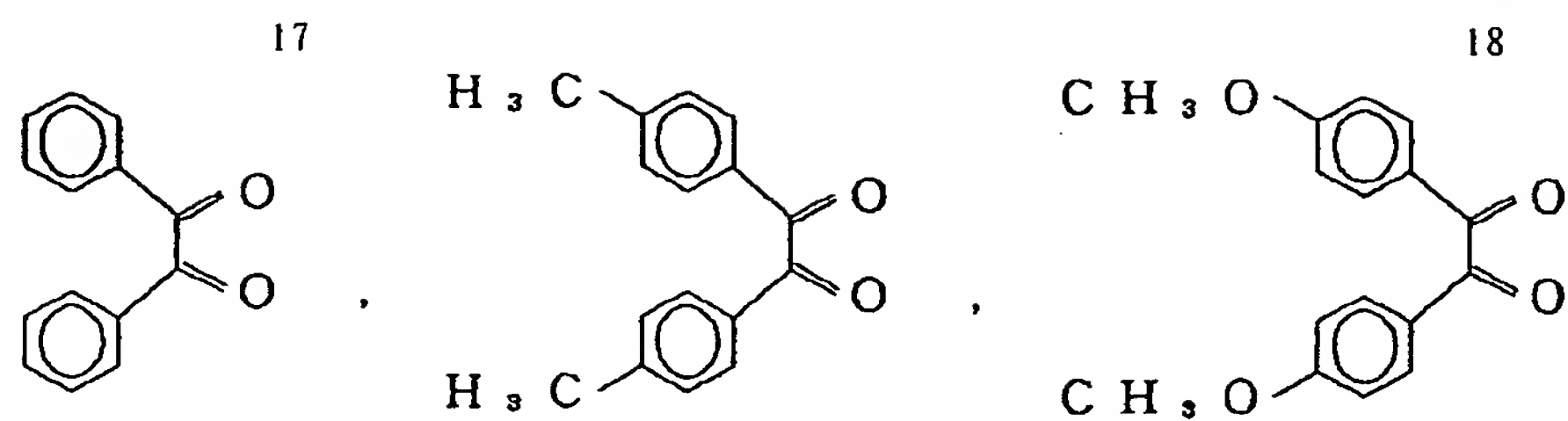
【0031】

【化8】

この反応でXとYが異なる場合、キノキサリン環同士の結合位置により、6, 6' - 体、6, 7' - 体、7, 7' - 体の構造異性体の混合物を生じる。ここで用いるジケトンとしては、

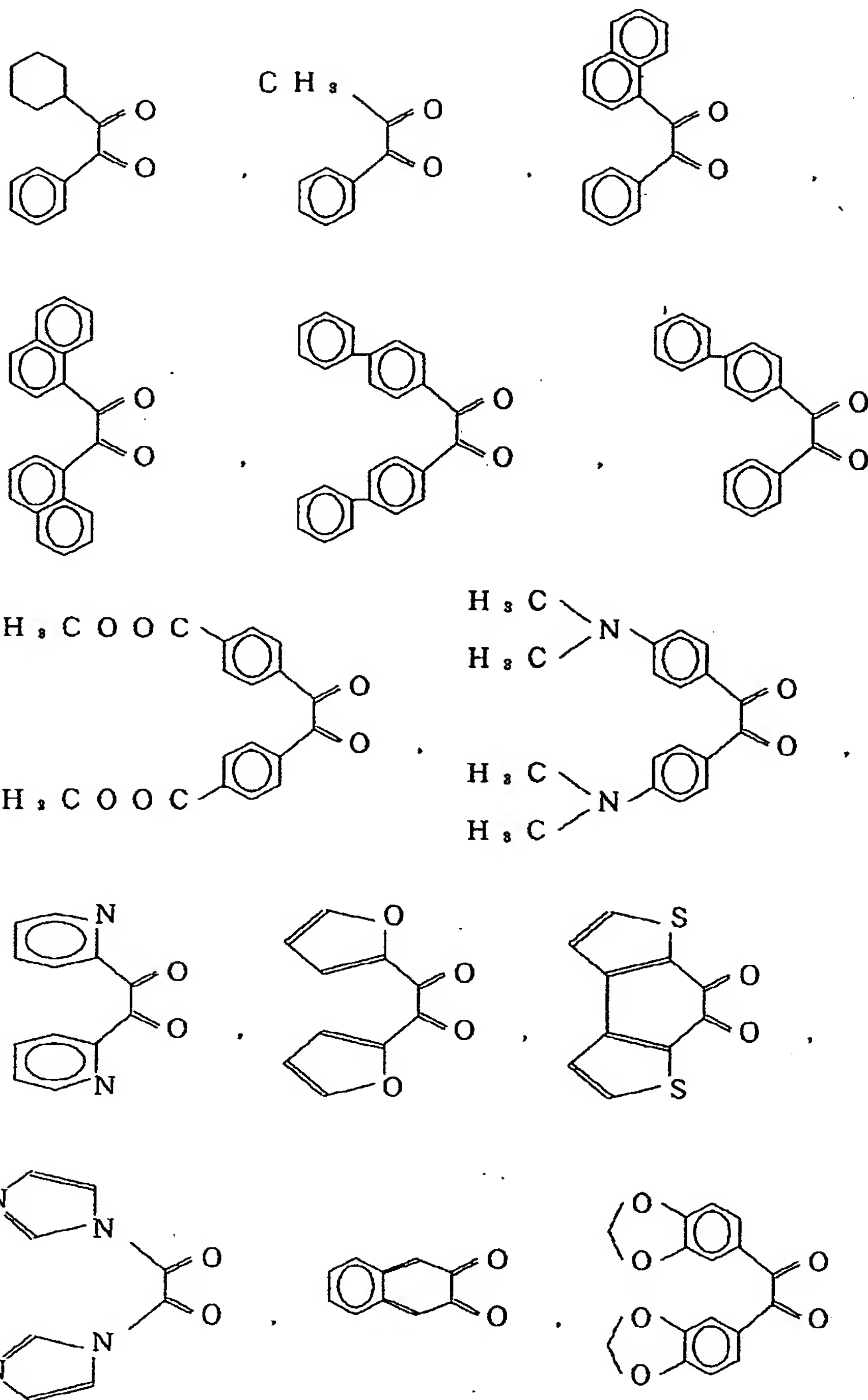
【0033】

【化9】



【0034】

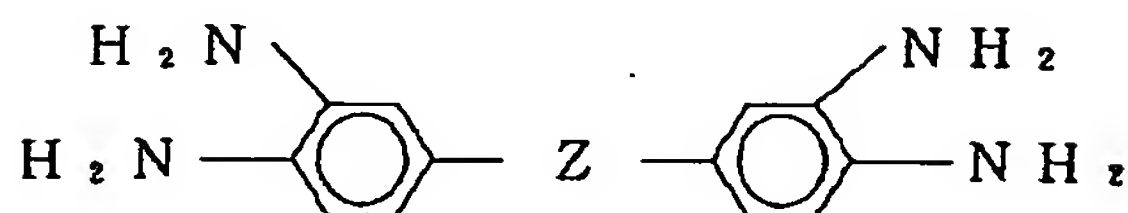
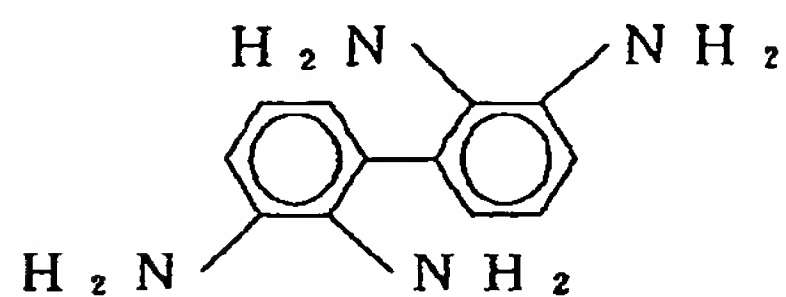
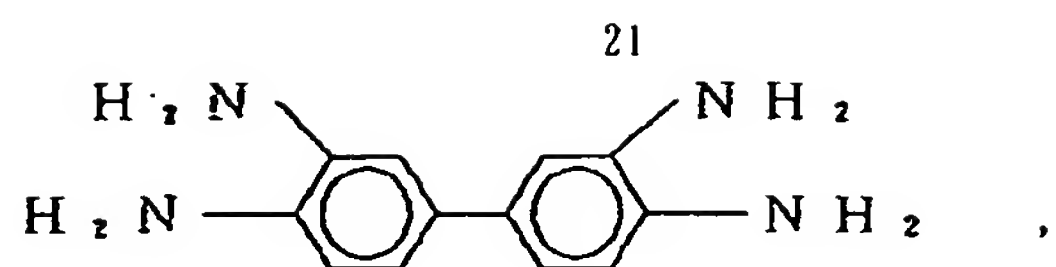
【化10】



【0035】が挙げられる。また、 α -フェニレンジアミン誘導体としては、

【0036】

【化 1 1】



(式中、Zは前記と同じである。)

【0037】が挙げられる。

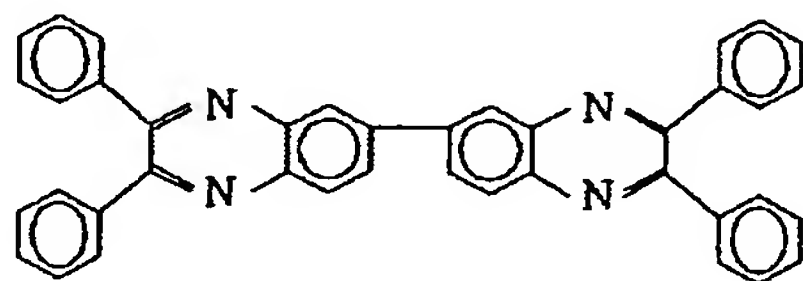
【0038】

【実施例】本発明を合成例、実施例及び比較例を用いて、さらに詳しく説明する。

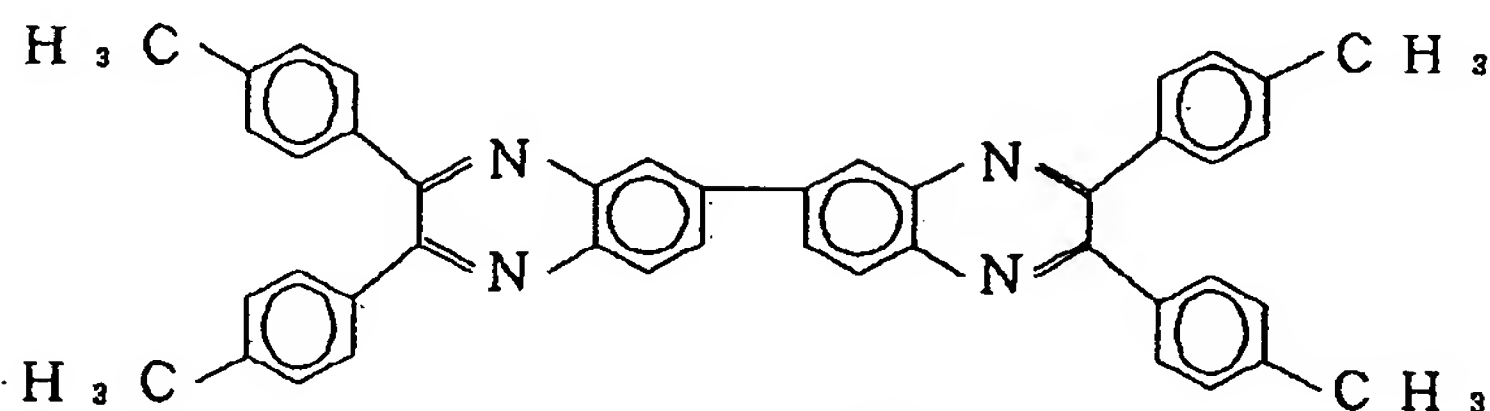
合成例1

【0039】

【化12】



【0040】2, 2', 3, 3'-テトラフェニルー



【0043】2, 2', 3, 3'-テトラ(p-トリル)-6, 6'-ジキノキサリンの合成
n-ブタノール40ミリリットルおよび酢酸20ミリリットルの混合溶液に3, 3'-ジアミノベンジン2.14 g (0.01モル)を溶かし、次いで酢酸20ミリリットルに4, 4'-ジメチルベンジル4.8 g (0.02モル)を溶かした温溶液を加え4時間、80℃で攪拌した。放冷後、生成した黄土色粉末を吸引濾過した。この黄土色粉末を冷やしたエタノールで洗浄して淡黄色粉末5.0 g (収率: 95% (0.0095モル))を得た。この黄色粉末の融点は334℃であった。得られた淡黄色粉末の質量分析の結果、 $m/z = 618$ (M')であった。また、プロトン核磁気共鳴 ($^1\text{H-NMR}$, 基準: TMS, 溶媒: DMSO, 測定波長: 400 MHz) 測定の

22

6, 6'-ジキノキサリンの合成

3, 3'-ジアミノベンジン2.14 g (0.01モル)とベンジル4.2 g (0.02モル)をクロロホルム中で8時間還流し、溶媒を濾別して黄土色粉末を得た。さらに、トルエンより再沈澱させて淡黄色粉末5.0 g (収率: 89% (0.0089モル))を得た。この淡黄色粉末の融点は312℃であった。得られた淡黄色粉末の質量分析の結果、 $m/z = 562$ (M')であった。また、プロトン核磁気共鳴 ($^1\text{H-NMR}$, 基準: テトラメチルシラン (TMS), 溶媒: ジメチルスルホキシド (DMSO), 測定波長: 400 MHz) 測定の結果、
 $\delta = 7.35 \sim 7.44$ ppm (m, 12H, フェニル基の3, 4位のH)
 $\delta = 7.52 \sim 7.57$ ppm (m, 8H, フェニル基の2位のH)
 $\delta = 8.3$ ppm (d, 2H, キノキサリン環の8位のH)
 $\delta = 8.45$ ppm (q, 2H, キノキサリン環の7位のH)

20 $\delta = 8.54$ ppm (d, 2H, キノキサリン環の5位のH)

であった。以上から、目的のキノキサリン化合物が合成されていることが確認された。なお、実施例においては上記淡黄色粉末を塩化メチレンを展開溶媒として用い、シリカゲルカラムで分離した精製物を用いた。

【0041】合成例2

【0042】

【化13】

結果、

$\delta = 2.35$ ppm (s, 12H, フェニル基の3位のH)

40 $\delta = 6.92 \sim 6.98$ ppm (m, 8H, フェニル基の3位のH)

$\delta = 7.46 \sim 7.53$ ppm (m, 8H, フェニル基の2位のH)

$\delta = 8.22$ ppm (d, 2H, キノキサリン環の8位のH)

$\delta = 8.37$ ppm (q, 2H, キノキサリン環の7位のH)

$\delta = 8.55$ ppm (d, 2H, キノキサリン環の5位のH)

50 であった。以上から、目的のキノキサリン化合物が合成

されていることが確認された。なお、実施例においては上記淡黄色粉末を塩化メチレンを展開溶媒として用い、シリカゲルカラムで分離した精製物を用いた。

【0044】合成例3～17

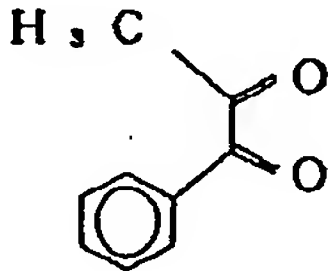
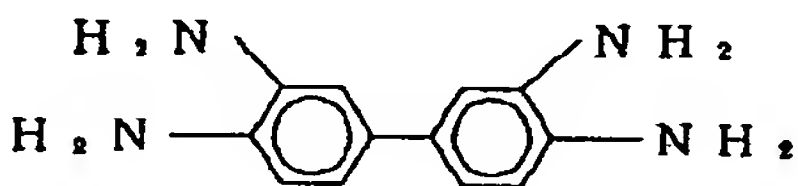
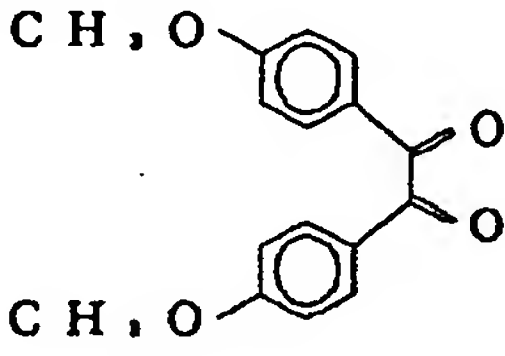
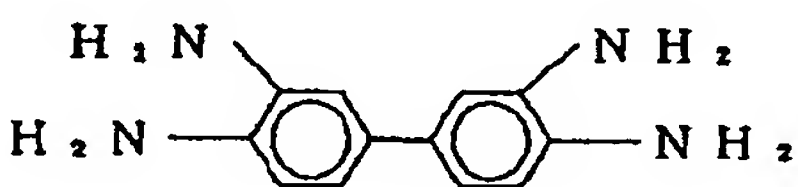
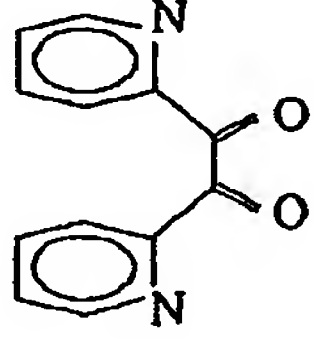
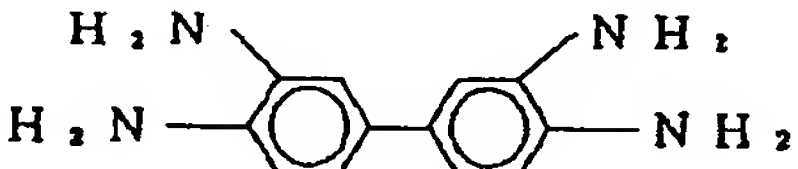
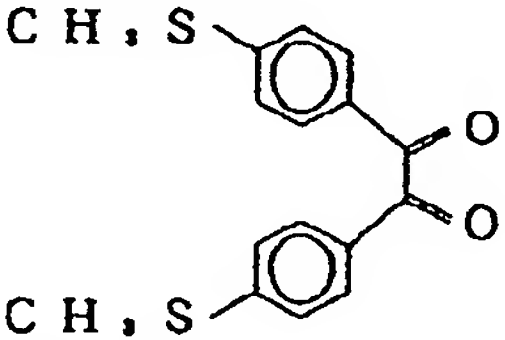
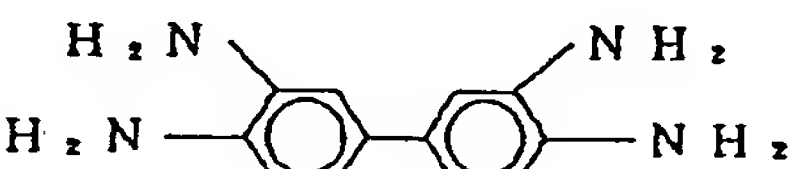
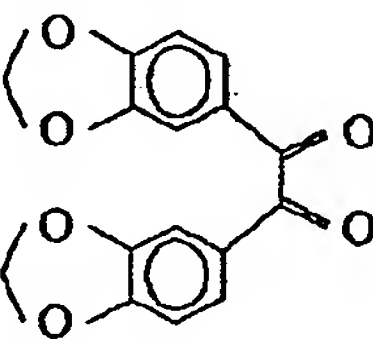
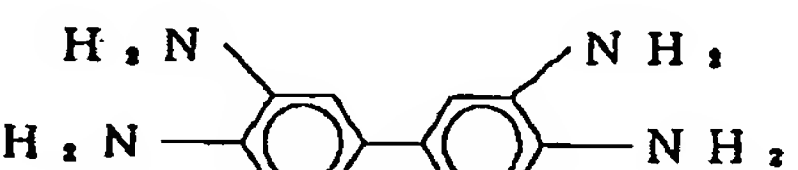
第1表に示したジケトンおよびテトラアミノ芳香族化合物を用いた以外は、合成例1と同様にして反応を行っ

た。得られたキノキサリン化合物を第2表に示す。但し、合成例7, 8, 9および12の化合物は昇華法により精製した。

【0045】

【表1】

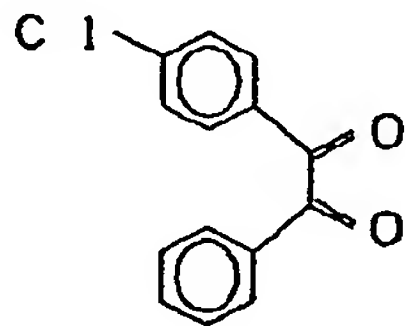
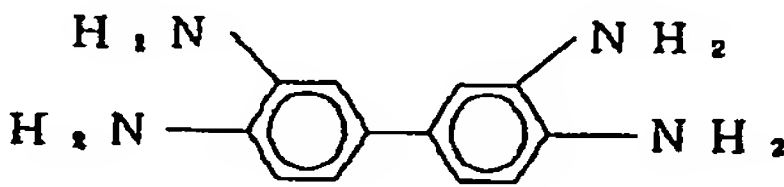
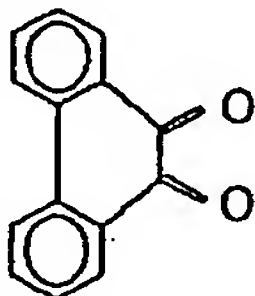
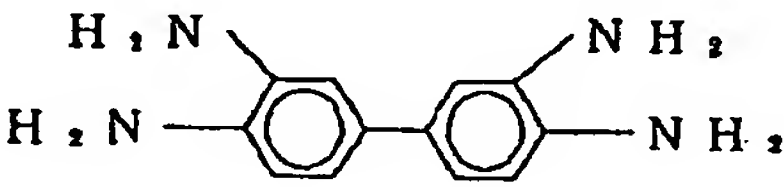
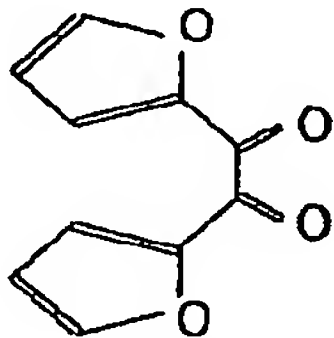
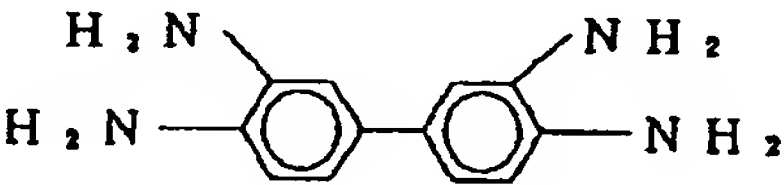
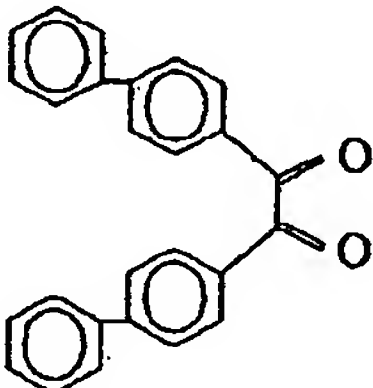
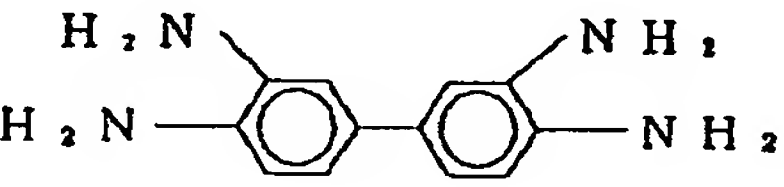
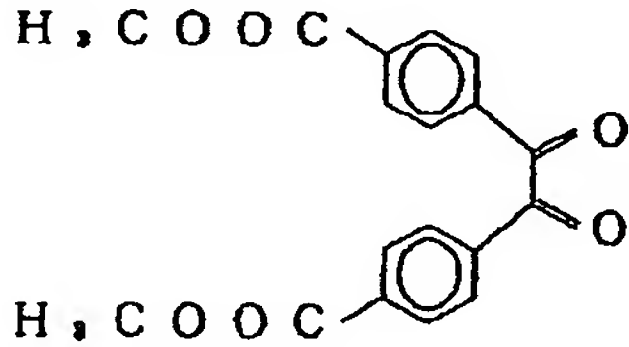
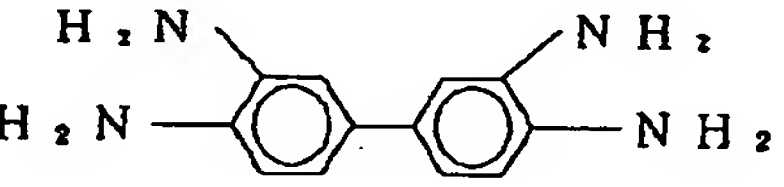
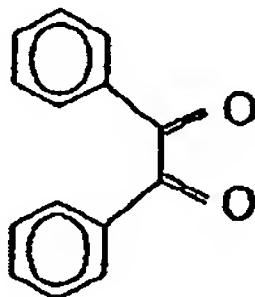
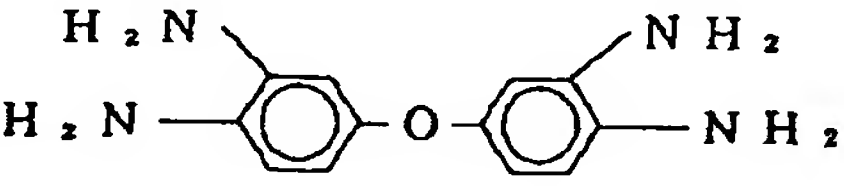
第1表(1)

	ジケトン	テトラアミノ芳香族化合物
合成例3		
合成例4		
合成例5		
合成例6		
合成例7		

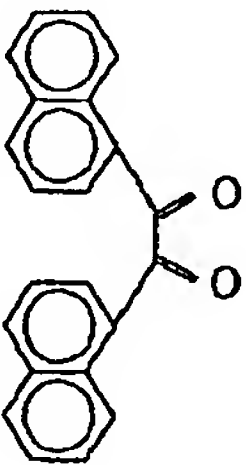
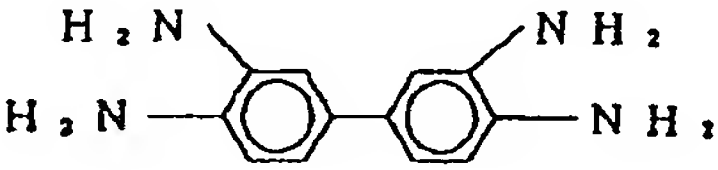
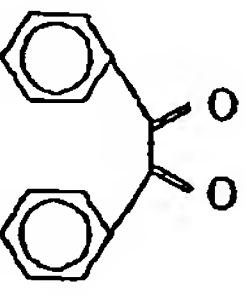
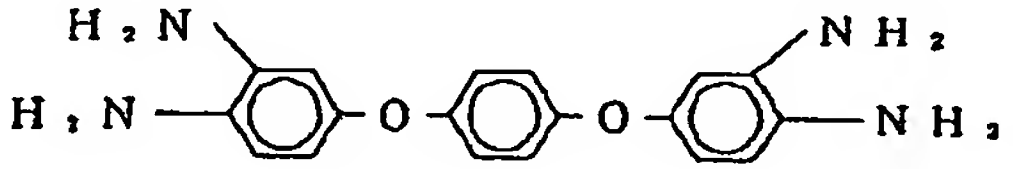
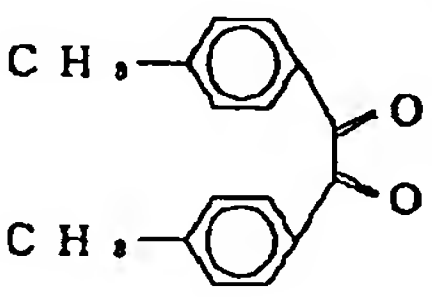
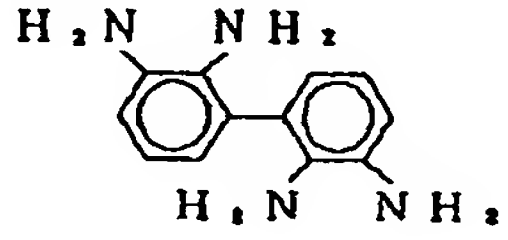
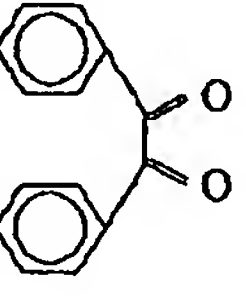
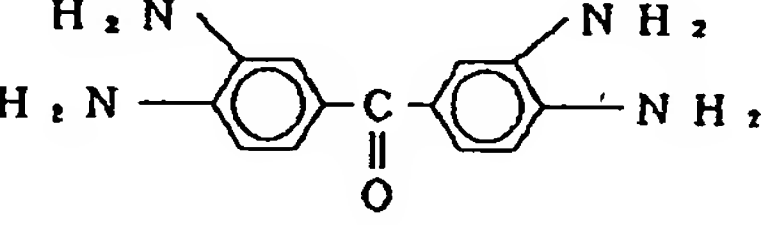
【0046】

【表2】

第 1 表 (2)

	ジケトン	テトラアミノ芳香族化合物
合成例 8		
合成例 9		
合成例 10		
合成例 11		
合成例 12		
合成例 13		

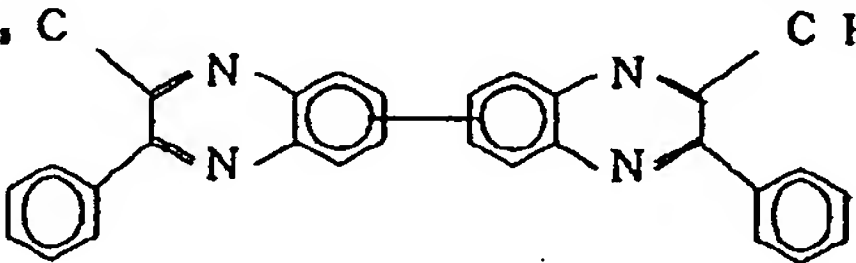
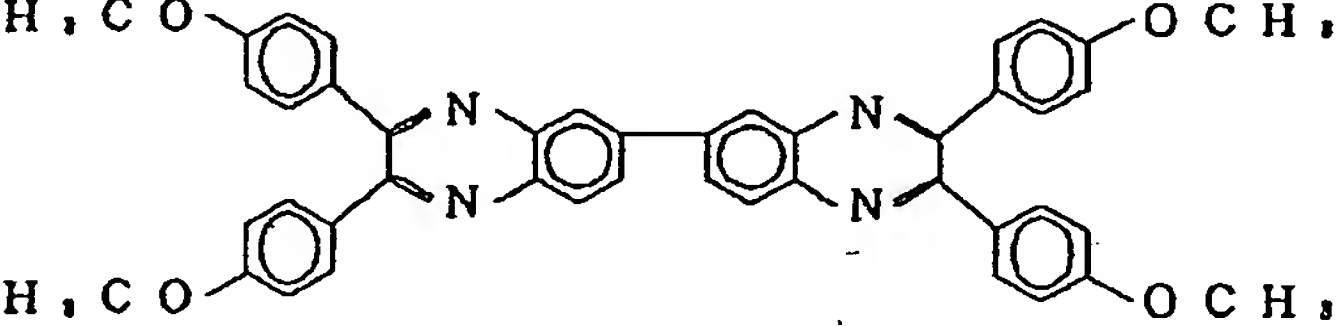

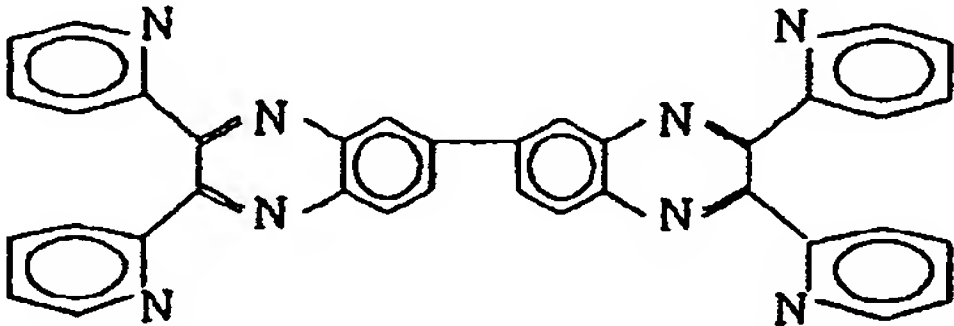
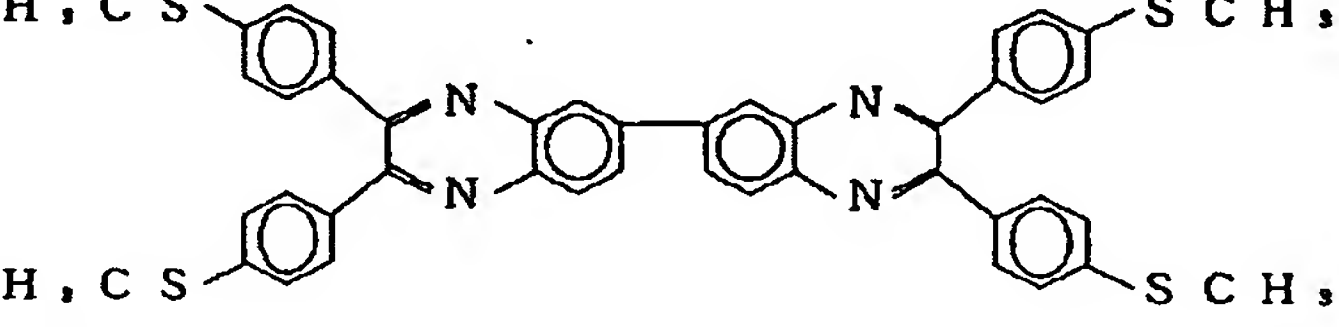

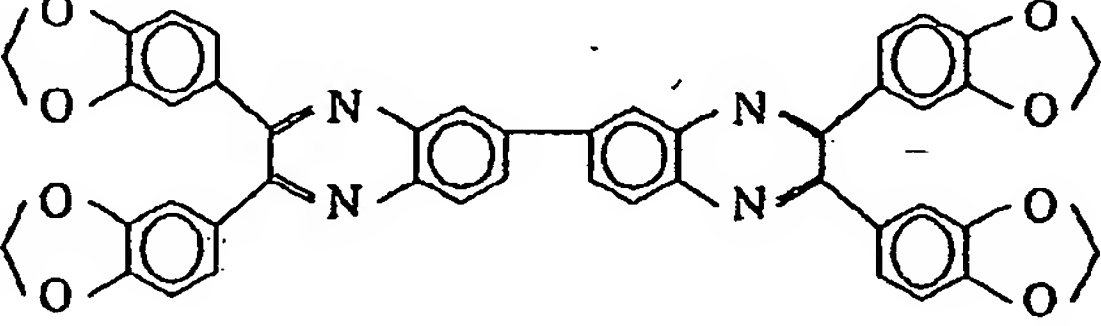
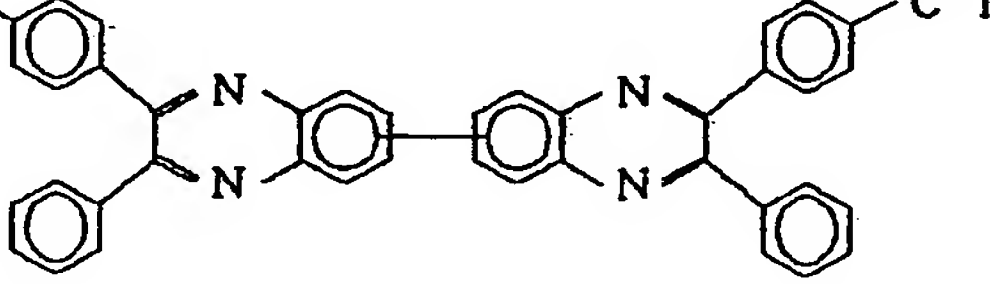
第1表(3)

	ジケトン	テトラアミノ芳香族化合物
合成例14		
合成例15		
合成例16		
合成例17		

【0048】

【表4】

第2表(1)

	キノキサリン化合物
合成例 3	H, C  CH, 6,6';6,7';7,7'- キノキサリン化合物 の混合物
合成例 4	H, CO  OCH, H, CO  OCH,
合成例 5	
合成例 6	H, CS  SCH, H, CS  SCH,
合成例 7	
合成例 8	Cl  Cl

【0049】

【表5】

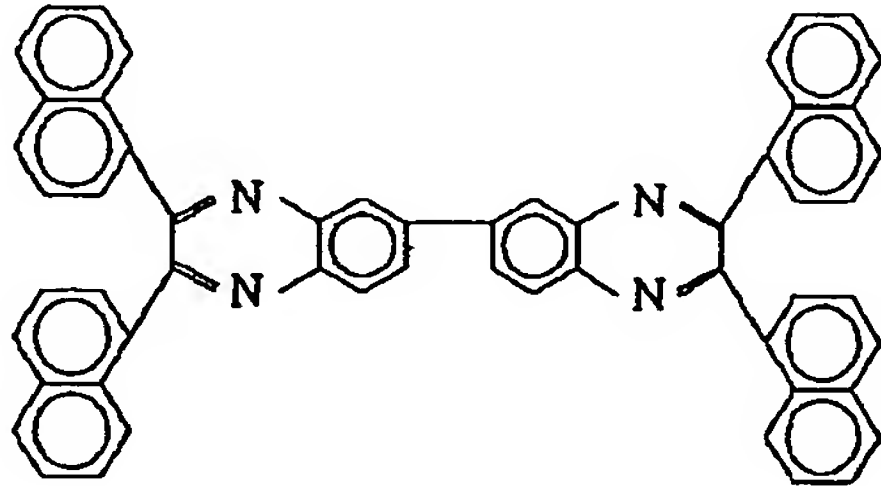
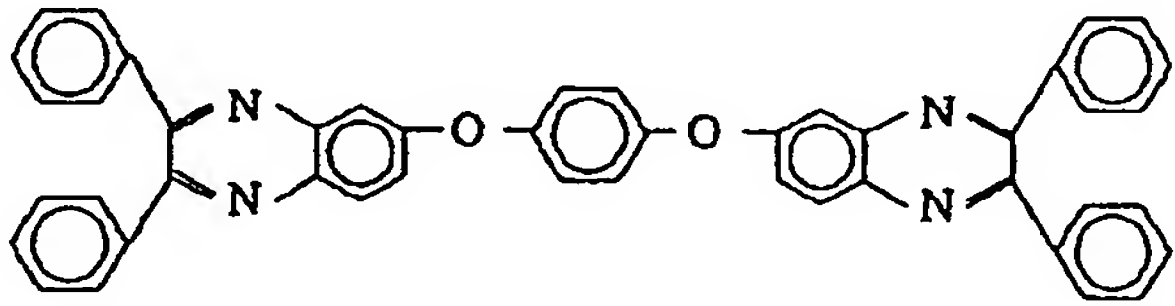
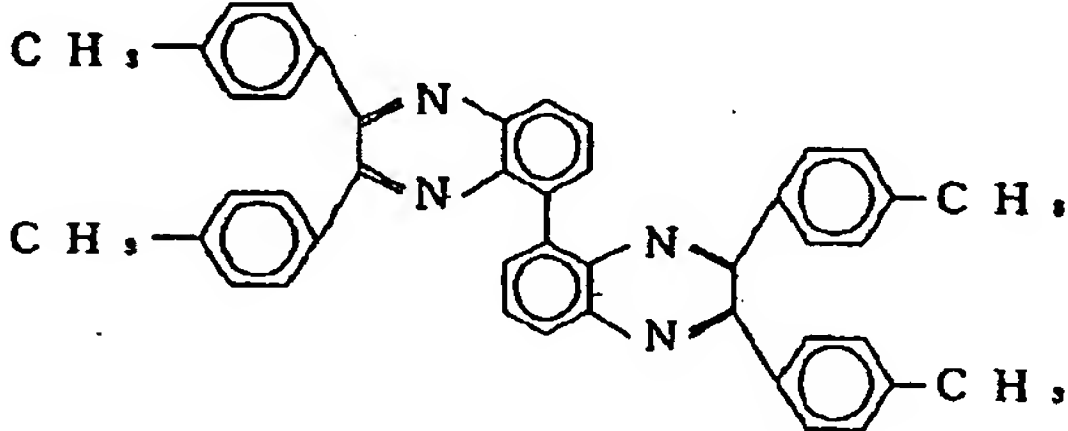
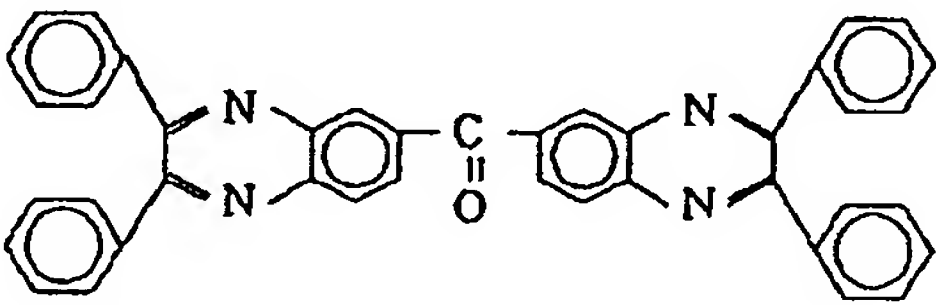
第 2 表 (2)

	キノキサリン化合物
合成例 9	
合成例 10	
合成例 11	
合成例 12	
合成例 13	

【 0 0 5 0 】

【 表 6 】

第 2 表 (3)

	キノキサリン化合物
合成例 14	
合成例 15	
合成例 16	
合成例 17	

【0051】実施例 1

膜厚 100 nm の ITO 透明電極が設けられているガラス基板 (25 mm × 75 mm × 1.1 mm : HOYA 社製) を透明支持基板とし、これをイソプロピルアルコールで 30 分間超音波洗浄し、さらに浸漬して洗浄した。この透明支持基板を乾燥窒素ガスで乾燥し、市販の真空蒸着装置の基板ホルダーに固定した。一方、モリブデン製抵抗加熱ポートに、N, N'-ジフェニル-N, N'-ビス (3-メチルフェニル) (1, 1'-ビフェニル) - 4, 4'-ジアミン (TPDA) 200 mg を入

熱ポートに通電して 220℃ まで加熱して、蒸着速度 0.1 ~ 0.3 nm/秒 で上記正孔注入層上に蒸着し、膜厚 40 nm の発光層を設けた。さらに、TPDQ の入った前記加熱ポートに通電して 314℃ まで加熱して、蒸着速度 0.1 nm/秒 で上記発光層上に蒸着し、膜厚 20 nm の電子注入層を設けた。なお、蒸着時の基板温度は室温であった。次に、真空層をあけ電子注入層上にステンレス鋼製のマスクを設置し、一方、モリブデン製抵抗加熱ポートにはマグネシウム 3 g, タングステン製の蒸着用バスケットに銀を 0.5 g 入れ、再度真空層を 2×10^{-4} Pa まで減圧した後、マグネシウム入りのポートに通電して、蒸着速度 1.5 ~ 2.0 nm/秒 でマグネシウムを蒸着すると共に、同時に銀のバスケットを加熱し蒸着速度 0.1 nm/秒 で銀を蒸着し、マグネシウムと銀の混合物からなる対向電極とすることにより、目的とする有機 EL 素子を作成した。この素子の ITO 電極を陽極、マグネシウムと銀の混合物からなる対向電極を陰極として、直流 10 ボルトを印加したところ電流密度 14 mA/cm² の電流が流れ、青色の発光が得られた。この発光の最大波長は 474 nm, 輝度は 230 cd/m², 発光

効率0.52ルーメン/Wであった。通電後50時間経ても電極表面の剥離や白濁化はなく、依然青色発光が認められた。

【0052】実施例2～13

TPDQの代わりに第3表に示す化合物を用い、蒸着時

の加熱温度を第3表に示すように変えた以外は、実施例1と同様にして素子を作製し評価を行った。得られた結果を第3表に示す。

【0053】

【表7】

第3表

	用いた 有機リン化合物	蒸着温度 (℃)	印加電圧 (V)	電流密度 (mA/cm ²)	発光輝度 (cd/m ²)
実施例2	合成例2	320	10	59	930
実施例3	合成例3	245	10	9	93
実施例4	合成例4	333	10	104	490
実施例5	合成例5	345	10	70	375
実施例6	合成例6	333	10	12	128
実施例7	合成例7	318	10	13	120
実施例8	合成例8	300	10	23	140
実施例9	合成例9	325	10	41	212
実施例10	合成例10	295	10	18	135
実施例11	合成例11	393	10	24	212
実施例12	合成例12	310	10	19	144
実施例13	合成例13	297	12	19	180

【0054】

【表8】

第3表 (続き)

	発光効率 (ルーメン/W)	発光ピーク波長 (nm)	電極の 付着性	素子の寿命 (時間)
実施例 2	0.53	474	良好	50時間以上
実施例 3	0.32	482	良好	50時間以上
実施例 4	0.15	483	良好	50時間以上
実施例 5	0.17	484	良好	50時間以上
実施例 6	0.33	483	良好	50時間以上
実施例 7	0.29	480	良好	25時間以上
実施例 8	0.19	478	良好	25時間以上
実施例 9	0.16	481	良好	25時間以上
実施例 10	0.24	474	良好	25時間以上
実施例 11	0.28	475	良好	25時間以上
実施例 12	0.20	474	良好	25時間以上
実施例 13	0.25	473	良好	50時間以上

【0055】実施例14

DPVBiの代わりにトリス(8-ヒドロキシキノリン)アルミニウムを用い、蒸着時の加熱ポート温度を280℃に変えた以外は、実施例1と同様にして素子を作製し評価を行った。この素子のITO電極を陽極、マグネシウムと銀の混合物からなる対向電極を陰極として、直流10ボルトを印加したところ電流密度48mA/cm²の電流が流れ、緑色の発光が得られた。この発光の最大波長は510nm、輝度は670cd/m²、発光効率0.44ルーメン/Wであった。通電後50時間経ても電極表面の剥離や白濁化はなく、依然緑色発光が認められた。

【0056】実施例15

DPVBiの代わりにTPDQを用い、蒸着時の加熱ポート温度を314℃に変えた以外は、実施例1と同様にして真空槽を4×10⁻⁴Paまで減圧した。その後、実施例1と同様にTPDAを60nm製膜し、さらにTPDQの入ったポートを314℃まで加熱し蒸着速度0.1nm/秒で60nm積層した。なお、蒸着時の基板温度は室温であった。次いで、真空槽を開けて、上記蒸着物の上にマスクを設置してから実施例1と同様の方法でマグネシウムと銀の混合物よりなる対向電極を蒸着積層して目的の素子を作製し評価を行った。この素子のITO電極を陽極、マグネシウムと銀の混合物からなる対向電極を陰極として、直流15ボルトを印加したところ電流密度14mA/cm²の電流が流れ、青紫色の発光が得

られた。この発光の最大波長は450nm、輝度は200cd/m²、発光効率0.3ルーメン/Wであった。通電後50時間経ても電極表面の剥離や白濁化はなく、依然青紫色発光が認められた。

【0057】実施例16

膜厚100nmのITO透明電極が設けられているガラス基板(25mm×75mm×1.1mm:HOYA社製)を透明支持基板とし、これをイソプロピルアルコールで30分間超音波洗浄し、さらに浸漬して洗浄した。この透明支持基板を乾燥窒素ガスで乾燥し、市販の真空蒸着装置の基板ホルダーに固定した。一方、モリブデン製抵抗加熱ポートに、TPDA200mgおよびポリ(N-ビニルカルバゾール)200mgをクロロベンゼン40ミリリットルに溶解して得られる溶液をスピニングして正孔注入層とした。さらに、DPVBi200mgおよび合成例2で得られた2, 2', 3, 3'-テトラ(p-トリル)-6, 6'-ジキノキサリン200mgをクロロホルム20gに溶解して得られた溶液をスピニングして発光層とした。上記スピニングは、7000回転/分で50秒間行い、膜厚は500±100Åであった。次に、得られた基板を真空蒸着装置の基板ホルダーに固定し、モリブデン製抵抗加熱ポートにマグネシウム3gを入れ、また別のモリブデン製抵抗加熱ポートにインジウムを1g入れ、再び真空層を4×10⁻⁴Paまで減圧した後、マグネシウム入りのポートに通電して、蒸着速度2~3nm/秒で

マグネシウムを蒸着すると共に、同時に別のモリブデン製ボートのインジウムを加熱し蒸着速度0.1~0.2 nm/秒でインジウムを蒸着し、マグネシウムとインジウムの混合物からなる対向電極とすることにより、目的とする有機EL素子を作成した。この素子のITO電極を陽極、マグネシウムとインジウムの混合物からなる対向電極を陰極として、直流12ボルトを印加したところ電流密度58 mA/cm²の電流が流れ、緑青色の発光が得られた。この発光の最大波長は480 nm、輝度は320 cd/m²、発光効率0.14ルーメン/Wであった。 10

通電後50時間経ても電極表面の剥離や白濁化はなく、依然緑青色発光が認められた。

【0058】実施例17~20

TPDQの代わりに第4表に示す化合物を用い、蒸着時の加熱温度を第4表に示すように変えた以外は、実施例1と同様にして素子を作製し評価を行った。得られた結果を第4表に示す。

【0059】

【表9】

第4表

	用いた 有機化合物	蒸着ボート温度 (℃)	印加電圧 (V)	電流密度 (mA/cm ²)	発光輝度 (cd/m ²)
実施例17	合成例14	300	12.5	14	221
実施例18	合成例15	340	12	16	169
実施例19	合成例16	190	11	9.1	110
実施例20	合成例17	286	10	24	88

【0060】

【表10】

第4表(続き)

	発光効率 (ルーメン/W)	発光ピーク波長 (nm)	電極の 付着性	素子の寿命 (時間)
実施例17	0.40	476	良好	25時間以上
実施例18	0.28	470	良好	25時間以上
実施例19	0.35	470	良好	50時間以上
実施例20	0.12	480	良好	25時間以上

【0061】比較例1

TPDQの代わりに市販の2,3-ジフェニルキノキサリンを塩化メチレンを展開溶媒としてシリカゲルカラムにより精製した試料を用い、蒸着時の加熱ボート温度を215℃に変えた以外は、実施例1と同様にして素子を作製して評価を行った。この素子のITO電極を陽極、マグネシウムとインジウムの混合物からなる対向電極を陰極として、直流14ボルトを印加したところ電流密度22 mA/cm²の電流が流れ、緑青色の発光が得られた。この発光の最大波長は484 nm、輝度は53 cd

/m²、発光効率0.05ルーメン/Wであった。通電後、電極表面の剥離が認められ、発光減衰が激しく0.5時間で消光した。

【0062】

【発明の効果】以上の如く、本発明の有機EL素子は、高輝度、高い発光効率、長寿命を有するものである。したがって、本発明の有機EL素子は、エレクトロニクス、表示素子などの化学工業において有効に利用することができる。

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(57) Abstract: Phosphorescent organometallic complexes comprising phenylquinolinato ligands are provided. High efficiency or-
ganic light emitting devices comprising these compounds are also described.



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PHOSPHORESCENT COMPOUNDS AND DEVICES COMPRISING THE SAME

5 FIELD OF THE INVENTION

The present invention pertains to organometallic compounds and efficient organic light emitting devices comprising the same.

BACKGROUND OF THE INVENTION

10 Electronic display currently is a primary means for rapid delivery of information. Television sets, computer monitors, instrument display panels, calculators, printers, wireless phones, handheld computers, etc. aptly illustrate the speed, versatility, and interactivity that is characteristic of this medium. Of the known electronic display technologies, organic light emitting devices (OLEDs) are of considerable interest for
15 their potential role in the development of full color, flat-panel display systems that may render obsolete the bulky cathode ray tubes still currently used in many television sets and computer monitors.

Generally, OLEDs are comprised of several organic layers in which at least one of the layers can be made to electroluminesce by applying a voltage across the device
20 (see, e.g., Tang, *et al.*, *Appl. Phys. Lett.* 1987, 51, 913 and Burroughes, *et al.*, *Nature*, 1990, 347, 359). When a voltage is applied across a device, the cathode effectively reduces the adjacent organic layers (i.e., injects electrons) and the anode effectively oxidizes the adjacent organic layers (i.e., injects holes). Holes and electrons migrate across the device toward their respective oppositely charged electrodes. When a hole

and electron meet on the same molecule, recombination is said to occur and an exciton is formed. Recombination of the hole and electron in luminescent compounds is accompanied by radiative emission, thereby producing electroluminescence.

Depending on the spin states of the hole and electron, the exciton which results from hole and electron recombination can have either a triplet or singlet spin state. Luminescence from a singlet exciton results in fluorescence whereas luminescence from a triplet exciton results in phosphorescence. Statistically, for organic materials typically used in OLEDs, one quarter of the excitons are singlets and the remaining three quarters are triplets (see, e.g., Baldo, *et al.*, *Phys. Rev. B*, 1999, 60,14422). Until the discovery that there were certain phosphorescent materials that could be used to fabricate practical electro-phosphorescent OLEDs (U.S. Pat. No. 6,303,238) and, subsequently, demonstration such that electro-phosphorescent OLEDs could have a theoretical quantum efficiency of up to 100% (i.e., harvesting all of both triplets and singlets), the most efficient OLEDs were typically based on materials that fluoresced. Fluorescent materials luminesce with a maximum theoretical quantum efficiency of only 25% (where quantum efficiency of an OLED refers to the efficiency with which holes and electrons recombine to produce luminescence), since the triplet to ground state transition of phosphorescent emission is formally a spin forbidden process. Electro-phosphorescent OLEDs have now been shown to have superior overall device efficiencies as compared with electro-fluorescent OLEDs (see, e.g., Baldo, *et al.*, *Nature*, 1998, 395, 151. and Baldo, *e.g.*, *Appl. Phys. Lett.* 1999, 75(3), 4).

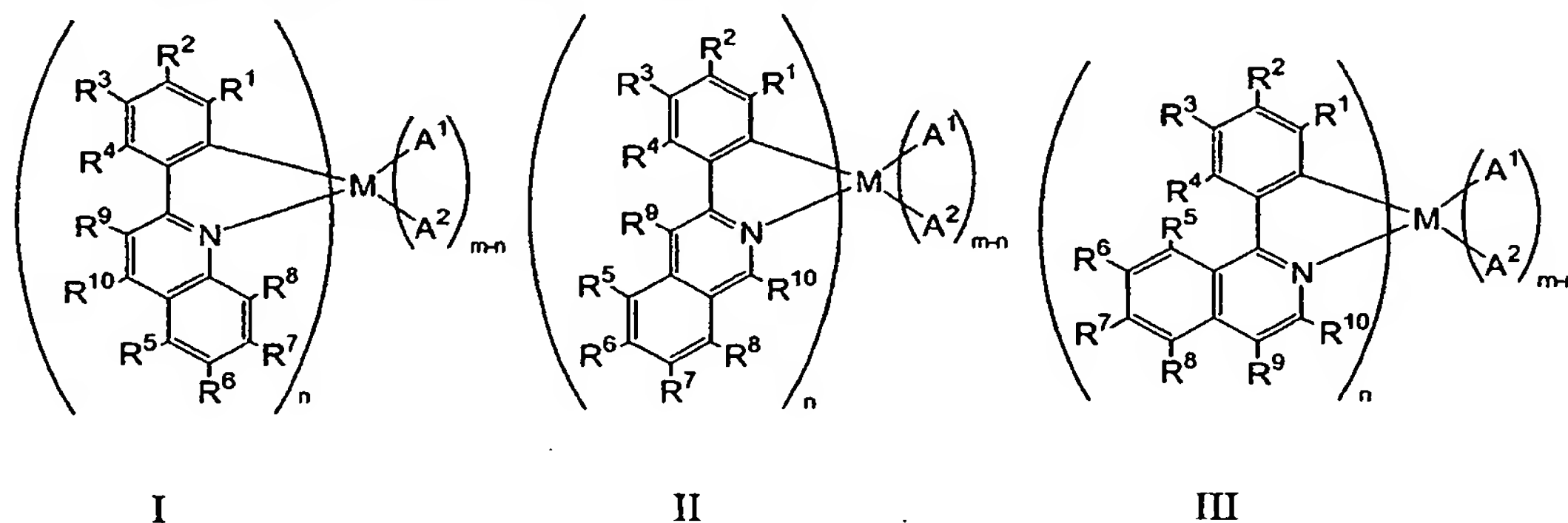
Due to strong spin-orbit coupling that leads to singlet-triplet state mixing, heavy metal complexes often display efficient phosphorescent emission from such triplets at room temperature. Accordingly, OLEDs comprising such complexes have been shown to have internal quantum efficiencies of more than 75% (Adachi, *et al.*, *Appl. Phys. Lett.*, 2000, 78,1704). Certain organometallic iridium complexes have been reported as having intense phosphorescence (Lamansky, *et al.*, *Inorganic Chemistry*, 2001, 40, 1704), and efficient OLEDs emitting in the green to red spectrum have been prepared with these complexes (Lamansky, *et al.*, *J. Am. Chem. Soc.*, 2001, 123, 4304). Red-emitting devices containing iridium complexes have been prepared according to U.S. Application Publication No. 2001/0019782. Phosphorescent heavy metal organometallic complexes and their respective devices have also been the subject of International Patent Application Publications WO 00/57676, WO 00/70655, and WO 01/41512; and U.S. Ser.

Nos. 09/274,609; 09/311,126; 09/452,346; 09/637,766; 60/283,814; and U.S. Ser. No. _____, filed October 16, 2001, entitled "Organometallic Compounds and Emission-Shifting Organic Electrophosphorescence" to Lamansky, *et al.*

Despite the recent discoveries of efficient heavy metal phosphors and the resulting advancements in OLED technology, there remains a need for even greater efficiency in devices. Fabrication of brighter devices that use less power and have longer lifetimes will contribute to the development of new display technologies and help realize the current goals toward full color electronic display on flat surfaces. The phosphorescent organometallic compounds, and the devices comprising them, described herein, help fulfill these and other needs.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides compounds of Formula I, II, or III:



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, F, Cl, Br, I, R¹¹, OR¹¹, N(R¹¹)₂, P(R¹¹)₂, P(OR¹¹)₂, POR¹¹, PO₂R¹¹, PO₃R¹¹, SR¹¹, Si(R¹¹)₃, B(R¹¹)₂, B(OR¹¹)₂, C(O)R¹¹, C(O)OR¹¹, C(O)N(R¹¹)₂, CN, NO₂, SO₂, SOR¹¹, SO₂R¹¹, SO₃R¹¹; and additionally, or alternatively, any one or more of R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and R¹⁰, together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each R^{11} is, independently, H, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, C_3 - C_{40} heteroaryl; wherein R^{11} is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R^{12} , OR^{12} , $N(R^{12})_2$, $P(R^{12})_2$, $P(OR^{12})_2$, POR^{12} , PO_2R^{12} , PO_3R^{12} , SR^{12} , $Si(R^{12})_3$, $B(R^{12})_2$, $B(OR^{12})_2$, $C(O)R^{12}$, $C(O)OR^{12}$, $C(O)N(R^{12})_2$, CN, NO_2 , SO_2 , SOR^{12} , SO_2R^{12} , or SO_3R^{12} ;

each R^{12} is, independently, H, C_1 - C_{20} alkyl, C_1 - C_{20} perhaloalkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, or C_3 - C_{40} heteroaryl;

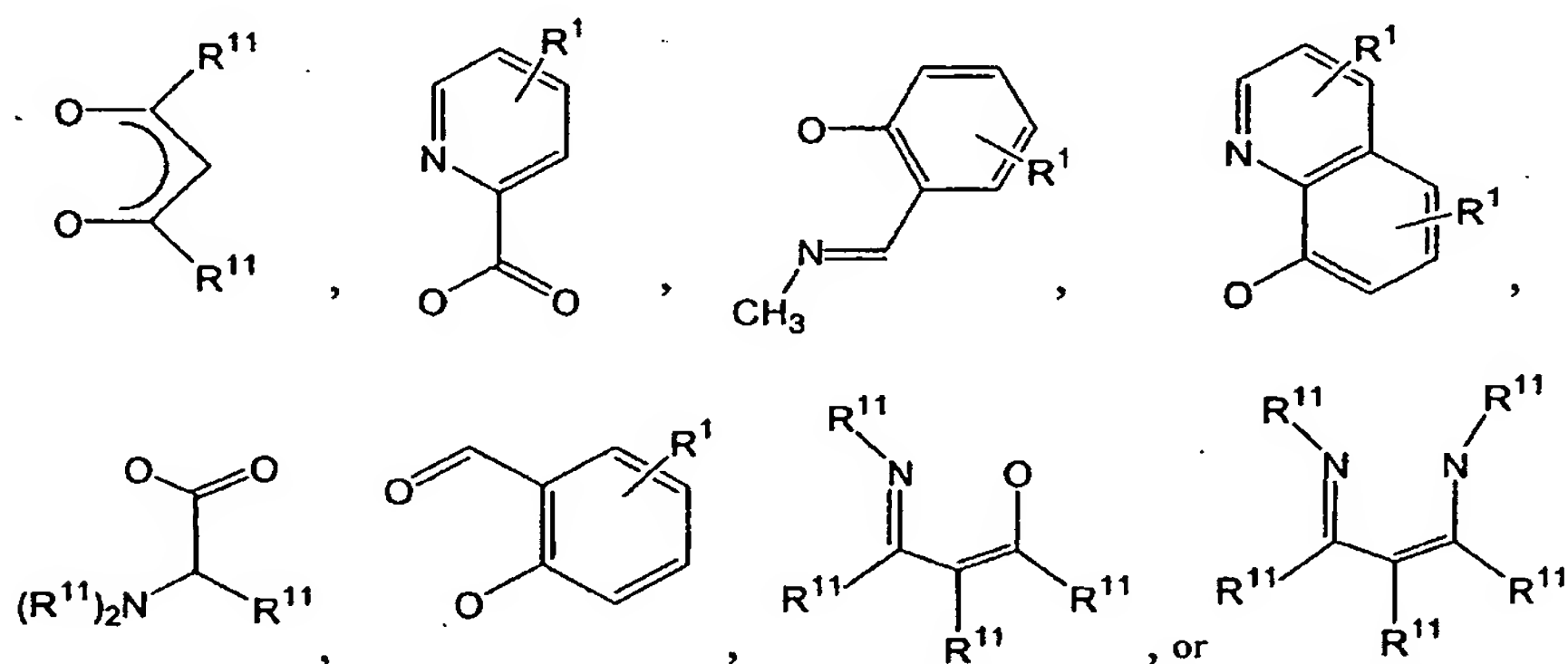
m is the formal charge of metal atom M;

n is 1, 2 or 3; and

wherein at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is not H in compounds of Formula I.

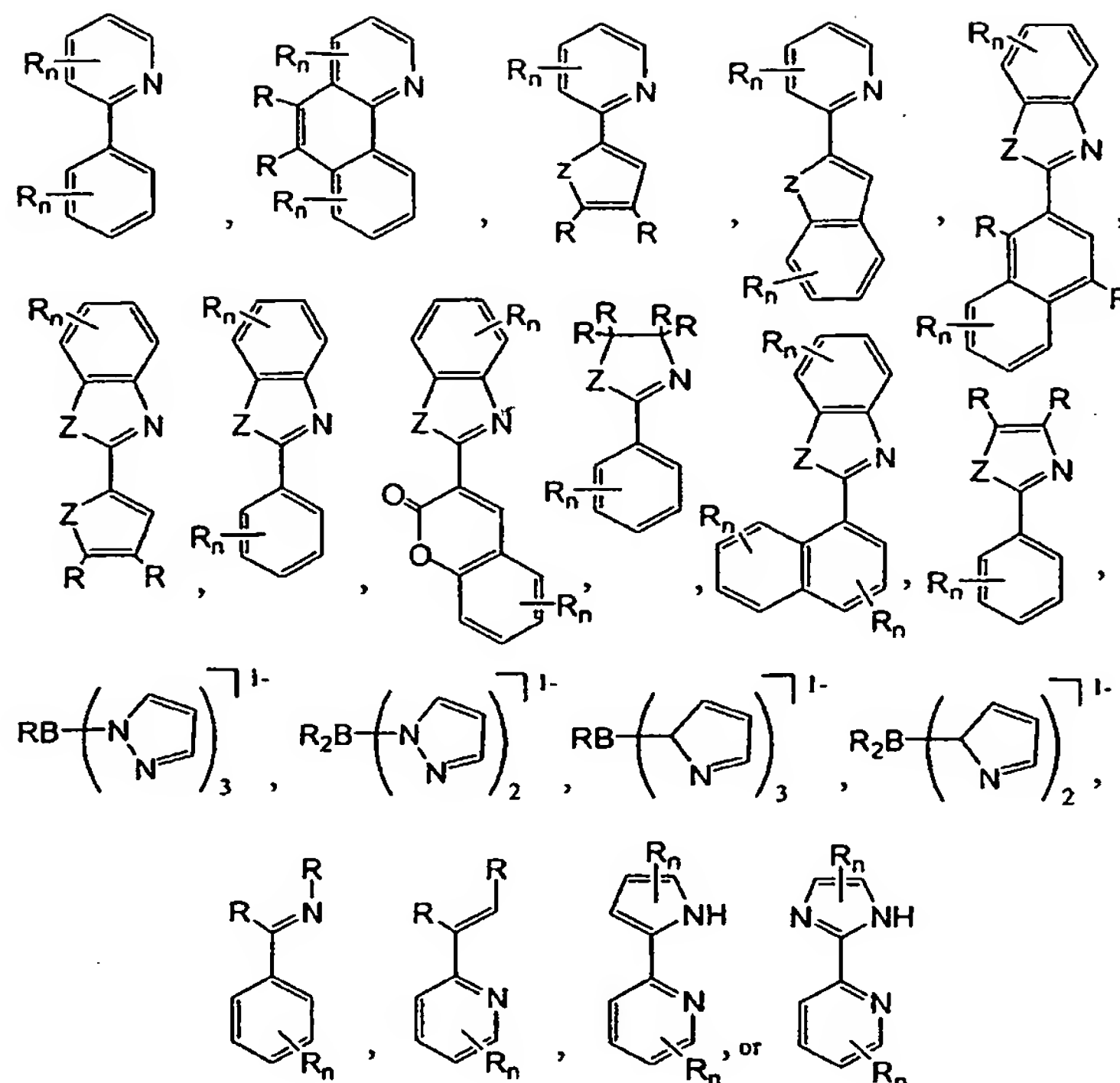
In some embodiments, M can be a heavy metal. In further embodiments, M can be Ir, Os, Pt, Pb, Re, or Ru; or M can be Ir; or M can be Pt. In further embodiments, A^1 and A^2 can be monodentate ligands which, in tum, can have a combined charge of (-1). In yet further embodiments, A^1 or A^2 can be F, Cl, Br, I, CO, CN, $CN(R^{11})$, SR^{11} , SCN, OCN, $P(R^{11})_3$, $P(OR^{11})_3$, $N(R^{11})_3$, NO, N_3 , or a nitrogen-containing heterocycle optionally substituted by one or more substituents X. In further embodiments, A^1 and A^2 can be covalently joined together to form a bidentate ligand, which can be monoanionic.

In some embodiments, the bidentate ligand can be



According to further embodiments, the bidentate ligand can coordinate through a carbon atom and a nitrogen atom. Further, the bidentate ligand can be a biaryl compound. In some embodiments, the bidentate ligand can be

25



wherein:

Z is O, S, or NR;

each R is, independently, R'' ; and

5 n is 0 to 5.

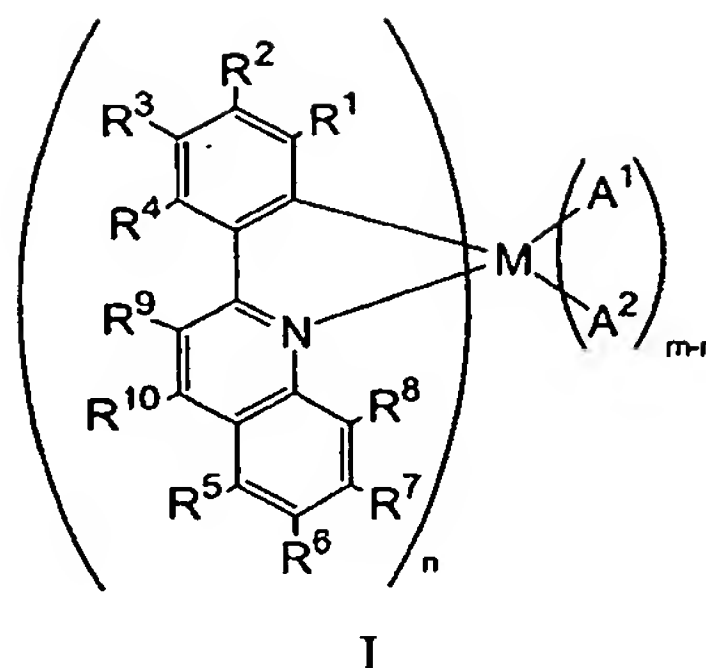
In some embodiments, bidentate ligand can be acetylacetonate.

In yet further embodiments, each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} can be, independently, H, CH_3 , CF_3 , OCH_3 , or F. In other embodiments, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is methyl. In other embodiments, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is trifluoromethyl. In other embodiments, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is methoxy. In other embodiments, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is fluoro. In other embodiments, at least one of said R^3 , R^4 , R^9 , and R^{10} is other than H.

According to some embodiments, compounds of the present invention can have a
15 photoluminescence maximum at a wavelength of from about 550 to about 700 nm.

The present invention further includes compositions comprising a compound of Formula I, II, or III as described above. Compositions can further comprise BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃, BAlq, Flrpic, or Irppy.

Also embodied by the present invention are compounds of Formula I



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand;

5 each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, an activating group, or a deactivating group; and additionally, or alternatively, any one or more of R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and R¹⁰, together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

10 each X is, independently, H, F, Cl, Br, I, R¹², OR¹², N(R¹²)₂, P(R¹²)₂, P(OR¹²)₂, POR¹², PO₂R¹², PO₃R¹², SR¹², Si(R¹²)₃, B(R¹²)₂, B(OR¹²)₂, C(O)R¹², C(O)OR¹², C(O)N(R¹²)₂, CN, NO₂, SO₂, SOR¹², SO₂R¹², or SO₃R¹²;

each R¹² is, independently, H, C₁-C₂₀ alkyl, C₁-C₂₀ perhaloalkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ heteroalkyl, C₃-C₄₀ aryl, or C₃-C₄₀ heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

wherein at least one of R³, R⁹, and R¹⁰ is an activating group, or wherein at least one of R³, R⁴, R⁹, and R¹⁰ is a deactivating group.

20 According to some embodiments of the compounds of Formula I, at least one of R³, R⁹, and R¹⁰ is an activating group. According to other embodiments of the compounds of Formula I at least one of R³, R⁴, R⁹, and R¹⁰ is a deactivating group. In some embodiments of the compounds of Formula I, activating groups can be alkyl, heteroalkyl, aryl, heteroaryl, alkoxy, aryloxy, hydroxy, mercapto, thiolato, amino, phosphino, alkylcarbonylamino, or arylcarbonylamino. In other embodiments of the

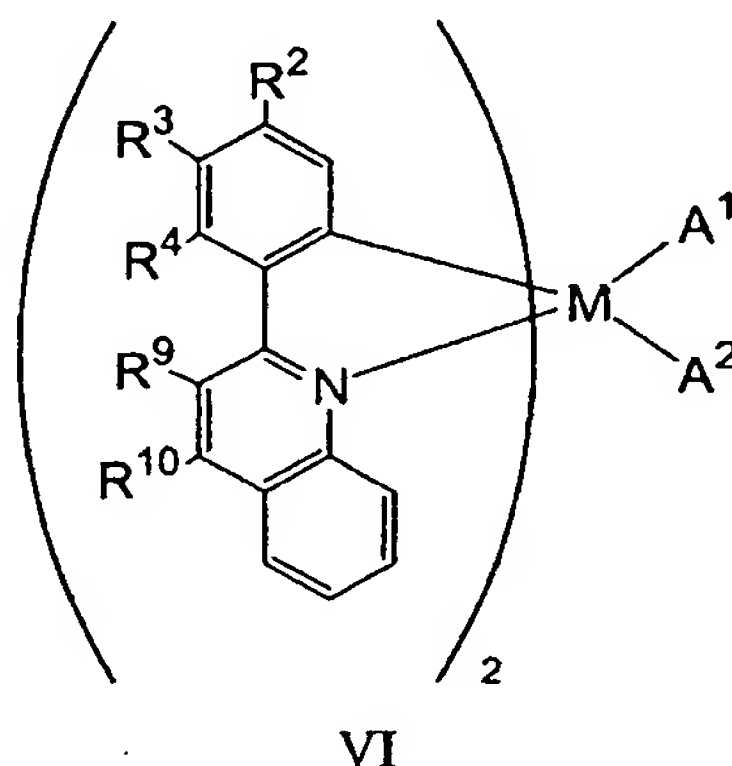
25

compounds of Formula I, activating groups can be methyl or methoxy. According to some embodiments of the compounds of Formula I, deactivating groups can be halo, cyano, nitro, aldehyde, alkylcarbonyl, arylcarbonyl, ammonium, perhaloalkyl, carboxylic acid, alkoxycarbonyl, aryloxycarbonyl, or sulfo. In other embodiments of the compounds of Formula I, deactivating group can be F or CF₃. In yet further
 5 compounds of Formula I, at least two of said R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ can be activating or deactivating groups.

Further embodiments of the compounds of Formula I include compounds where A¹ and A² are covalently joined together to form a bidentate ligand. The bidentate ligand
 10 can be monoanionic. The bidentate ligand can be acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate. In some embodiments, the bidentate ligand is acetylacetonate.

In yet further embodiments of the compounds of Formula I, M can be a heavy metal. In still further embodiments, M can be Ir, Os, Pt, Pb, Re, or Ru; or M can be Ir; or
 15 M can be Pt.

The present invention further includes compounds of Formula VI



wherein:

- 20 M is a metal atom;
 each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand; and
 R⁴ is F; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or
 25 R⁴ is OCH₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

5 R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

10 R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each, independently, H, an activating group or deactivating group; or

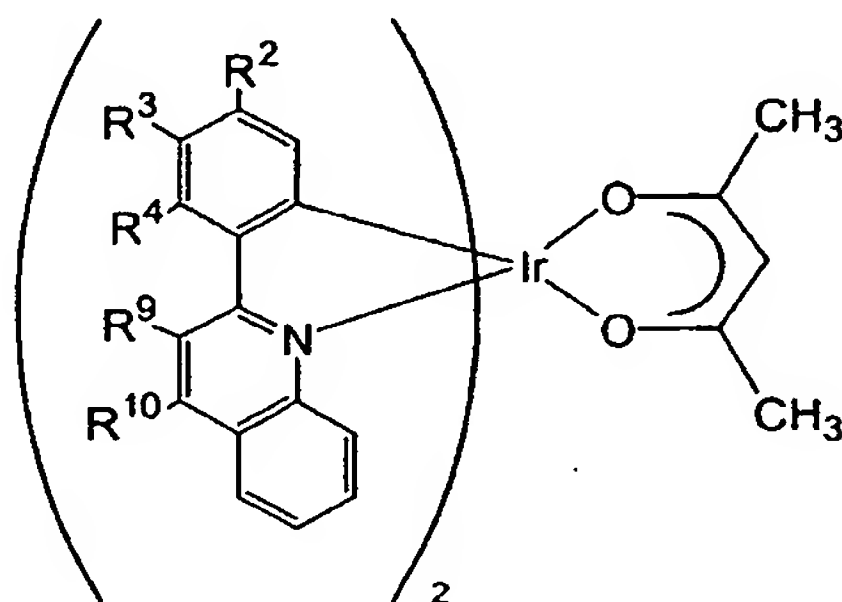
R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each, independently, H, an activating group or deactivating group; or

15 R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each, independently, H, an activating group or deactivating group.

According to some embodiments of the compounds of Formula VI, A^1 and A^2 can be covalently joined together to form a bidentate ligand. In other embodiments of the compounds of Formula VI, the bidentate ligand can be monoanionic. In further
20 embodiments of the compounds of Formula VI, bidentate ligand can be acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate. In yet further embodiments of the compounds of Formula VI, bidentate ligand can be acetylacetonate.

In some embodiments of the compounds of Formula VI, M can be a heavy metal;
25 or M can be Ir, Os, Pt, Pb, Re, or Ru; or M can be Ir; or M can be Pt.

The present invention further includes compounds of Formula IV



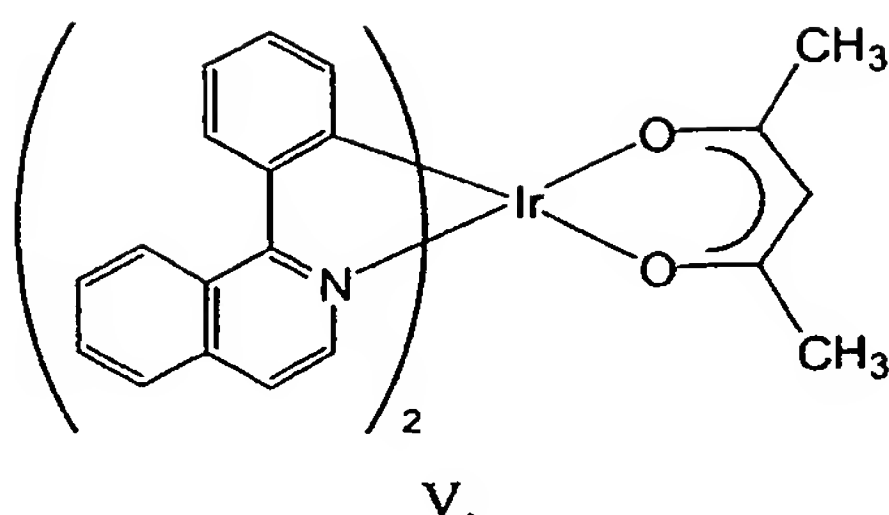
IV

wherein:

- R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 5 R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 10 R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H; or
 R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H; or
 R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H; or
 R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

In some embodiments of the compounds of Formula IV, R^4 is F; and R^2 , R^3 , R^9 ,
 15 and R^{10} are each H. In other embodiments of the compounds of Formula IV, R^4 is
 OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H. In other embodiments of the compounds of
 Formula IV, R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H. In other embodiments of
 the compounds of Formula IV, R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H. In other
 embodiments of the compounds of Formula IV, R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are
 20 each H. In other embodiments of the compounds of Formula IV, R^3 is CF_3 ; and R^2 , R^4 ,
 R^9 , and R^{10} are each H. In other embodiments of the compounds of Formula IV, R^2 is
 CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H. In other embodiments of the compounds of
 Formula IV, R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H. In other
 embodiments of the compounds of Formula IV, R^4 and R^{10} are each CH_3 ; and R^2 , R^3 ,
 25 and R^9 are each H. In other embodiments of the compounds of Formula IV, R^9 is CH_3 ;
 and R^2 , R^3 , R^4 , and R^{10} are each H. In other embodiments of the compounds of Formula
 IV, R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

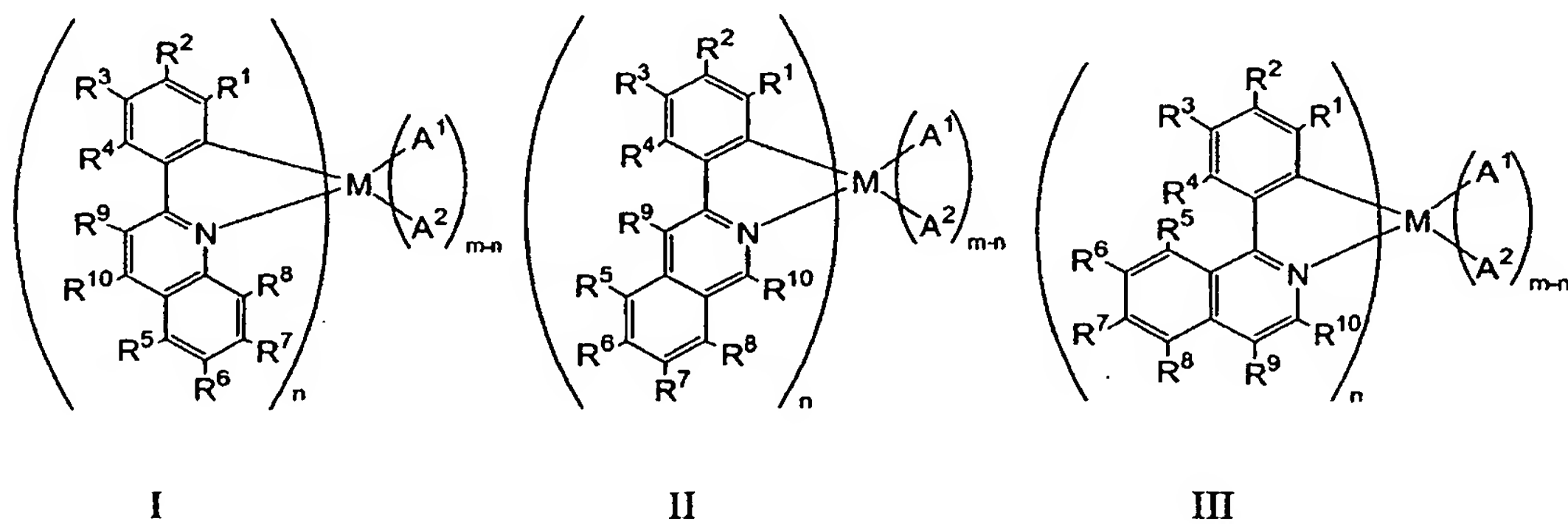
The present invention further embodies compounds of Formula V



The present invention further provides methods of increasing the wavelength of a photoluminescence maximum for compounds of the present invention, said methods comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is an activating group that influences the HOMO energy level of said compound, or at least one of said substituents is a deactivating group that influences the LUMO energy level of said compound.

The present invention further provides methods of decreasing the wavelength of a photoluminescence maximum for compounds of the present invention, said methods comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is a deactivating group that influences the HOMO energy level of said compound, or at least one of said substituents is an activating group that influences the LUMO energy level of said compound.

The present invention further includes organic light emitting devices comprising a compound of Formula I, II, or III



wherein:

M is a metal atom;

each A^1 and A^2 is, independently, a monodentate ligand; or A^1 and A^2 are covalently joined together to form a bidentate ligand;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9$, and R^{10} is, independently, H, F, Cl, Br, I, R^{11} , OR^{11} , $N(R^{11})_2$, $P(R^{11})_2$, $P(OR^{11})_2$, POR^{11} , PO_2R^{11} , PO_3R^{11} , SR^{11} , $Si(R^{11})_3$, $B(R^{11})_2$, $B(OR^{11})_2$, $C(O)R^{11}$, $C(O)OR^{11}$, $C(O)N(R^{11})_2$, CN, NO_2 , SO_2 , SOR^{11} , SO_2R^{11} , SO_3R^{11} ; and additionally, or alternatively, any one or more of R^1 and R^2 , or R^2 and R^3 , or R^3 and R^4 , or R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 , or R^9 and R^{10} , together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each R^{11} is, independently, H, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, C_3 - C_{40} heteroaryl; wherein R^{11} is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R^{12} , OR^{12} , $N(R^{12})_2$, $P(R^{12})_2$, $P(OR^{12})_2$, POR^{12} , PO_2R^{12} , PO_3R^{12} , SR^{12} , $Si(R^{12})_3$, $B(R^{12})_2$, $B(OR^{12})_2$, $C(O)R^{12}$, $C(O)OR^{12}$, $C(O)N(R^{12})_2$, CN, NO_2 , SO_2 , SOR^{12} , SO_2R^{12} , or SO_3R^{12} ;

each R^{12} is, independently, H, C_1 - C_{20} alkyl, C_1 - C_{20} perhaloalkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, or C_3 - C_{40} heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

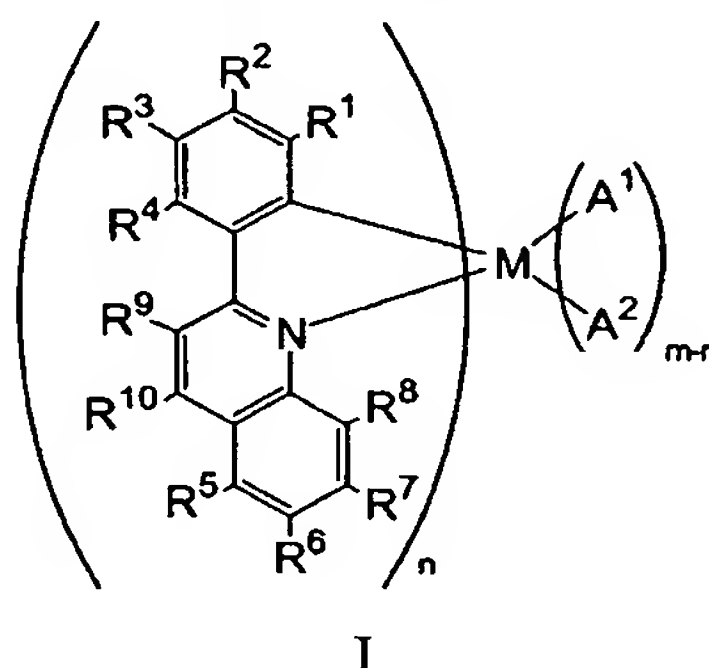
wherein at least one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9$, and R^{10} is not H in compounds of Formula I.

According to some embodiments, devices can have compounds of Formula I, Formula II, or Formula III. In other embodiments, device can include an emissive layer comprising one or more compounds of the present invention. In further embodiments, the emissive layer consists essentially of one or more compounds of the present invention. In other embodiments, the emissive layer can comprise host material doped with compounds of the present invention. In some embodiments, compound of the present invention comprise from about 1 to about 20 wt% of the emissive layer. In other embodiments, host material comprises BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃ or BAq. In yet other embodiments, the emissive layer further comprises FIrpic or Irppy.

According to some embodiments, devices have an electroluminescence maximum of from about 550 to about 700 nm. In other embodiments, devices emit a color having

color index coordinates (CIE) of from about 0.5 to about 0.8 for x and about 0.2 to about 0.5 for y . In yet further embodiments, devices have an external quantum efficiency greater than about 4% at a brightness greater than about 10 cd/m². In other embodiments, devices have an external quantum efficiency greater than about 4% at a
 5 brightness greater than about 100 cd/m².

In some embodiments, the present invention further provides organic light emitting devices comprising a compound of Formula I



wherein:

M is a metal atom;

10 each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, an activating group, or a deactivating group; and additionally, or alternatively, any one or more of R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and
 15 R¹⁰, together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R¹², OR¹², N(R¹²)₂, P(R¹²)₂, P(OR¹²)₂, POR¹², PO₂R¹², PO₃R¹², SR¹², Si(R¹²)₃, B(R¹²)₂, B(OR¹²)₂, C(O)R¹², C(O)OR¹²,
 20 C(O)N(R¹²)₂, CN, NO₂, SO₂, SOR¹², SO₂R¹², or SO₃R¹²;

each R¹² is, independently, H, C₁-C₂₀ alkyl, C₁-C₂₀ perhaloalkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ heteroalkyl, C₃-C₄₀ aryl, or C₃-C₄₀ heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

wherein at least one of R^3 , R^9 , and R^{10} is an activating group, or wherein at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group.

In some such embodiments, at least one of R^3 , R^9 , and R^{10} is an activating group. In other such embodiments, at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group. In further such embodiments, activating groups can be alkyl, heteroalkyl, aryl, heteroaryl, alkoxy, aryloxy, hydroxy, mercapto, thiolato, amino, phosphino, alkylcarbonylamino, or arylcarbonylamino. In yet further such embodiments, activating groups can be methyl or methoxy. According to some such embodiments, deactivating groups can be halo, cyano, nitro, aldehyde, alkylcarbonyl, arylcarbonyl, ammonium, perhaloalkyl, carboxylic acid, alkoxycarbonyl, aryloxycarbonyl, or sulfo. In other such embodiments, deactivating groups can be F or CF_3 . In yet further such embodiments, at least two of said R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} are activating or deactivating groups.

According to some such embodiments, A^1 and A^2 can be covalently joined together to form a bidentate ligand. In some such embodiments, bidentate ligand can be monoanionic. In some such embodiments, bidentate ligand can be acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate. In some embodiments, bidentate ligand is acetylacetonate.

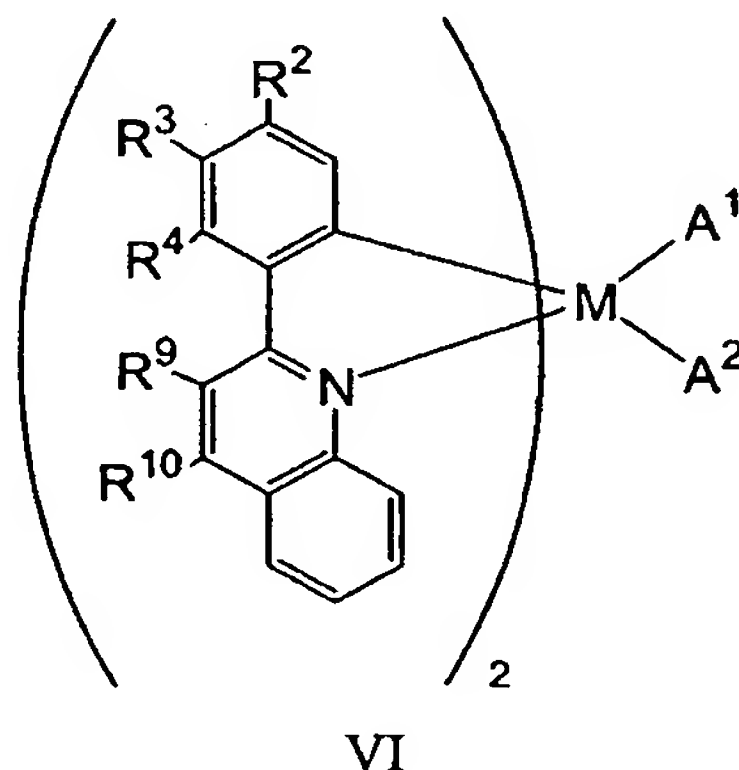
According to some such embodiments, M can be a heavy metal. In other such embodiments, M can be Ir, Os, Pt, Pb, Re, or Ru; or M can be Ir; or M can be Pt.

In some such embodiments, devices can include an emissive layer comprising compounds of the present invention. In some such embodiments, the emissive layer consists essentially of compounds of the present invention. In other such embodiments, the emissive layer comprises host material doped with compounds of the present invention. In further of such embodiments, compounds of the present invention can comprise from about 1 to about 20 wt% of the emissive layer. In some such embodiments, host material comprises BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃ or BAlq. In other such embodiments, the emissive layer further comprises FIrpic or Irppy.

According to some such embodiments, devices can have an electroluminescence maximum of from about 550 to about 700 nm. In other embodiments, color emitted from such devices can have color index coordinates (CIE) of from about 0.5 to about 0.8 for x and about 0.2 to about 0.5 for y. In some embodiments, such devices can have an external quantum efficiency greater than about 4% at a brightness greater than about 10

cd/m². In other such embodiments, such devices can have an external quantum efficiency greater than about 4% at a brightness greater than about 100 cd/m².

Further embodiments of the present invention include organic light emitting devices comprising compounds of Formula VI



5 wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand; and

10 R⁴ is F; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is OCH₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R³ is OCH₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

15 R² is OCH₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is CF₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

20 R³ is CF₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² is CF₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² and R⁴ are each F; and R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

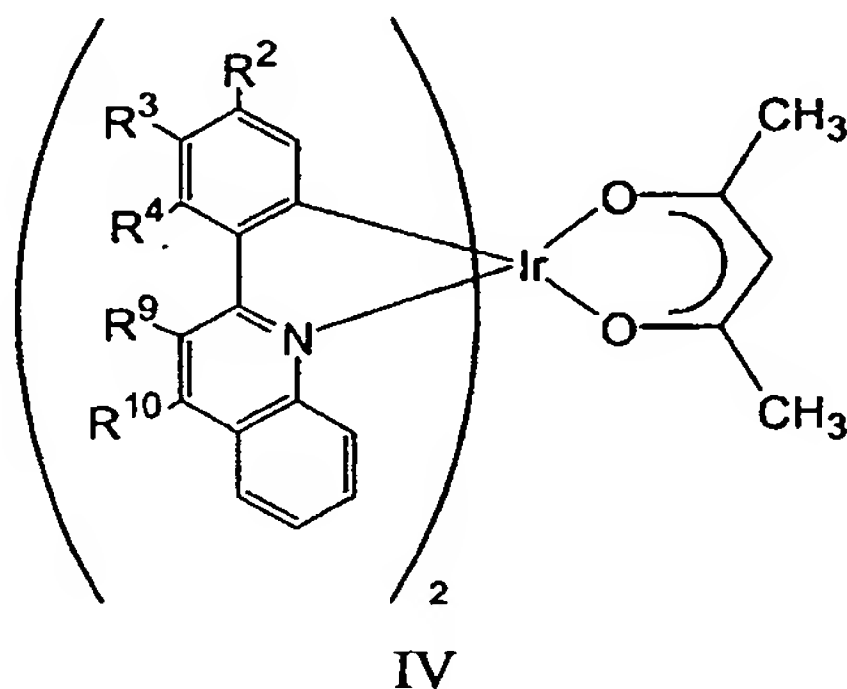
R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each, independently, H, an activating group or deactivating group.

5 According to some such embodiments, A^1 and A^2 can be covalently joined together to form a bidentate ligand. In other such embodiments, bidentate ligand can be monoanionic. In some such embodiments, bidentate ligand is acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate. In yet other such embodiments, bidentate ligand can be acetylacetonate.

10 In some such embodiments, M can be a heavy metal; or M can be Ir, Os, Pt, Pb, Re, or Ru; or M can be Ir; or M can be Pt.

The present invention further includes organic light emitting devices comprising compounds of Formula IV

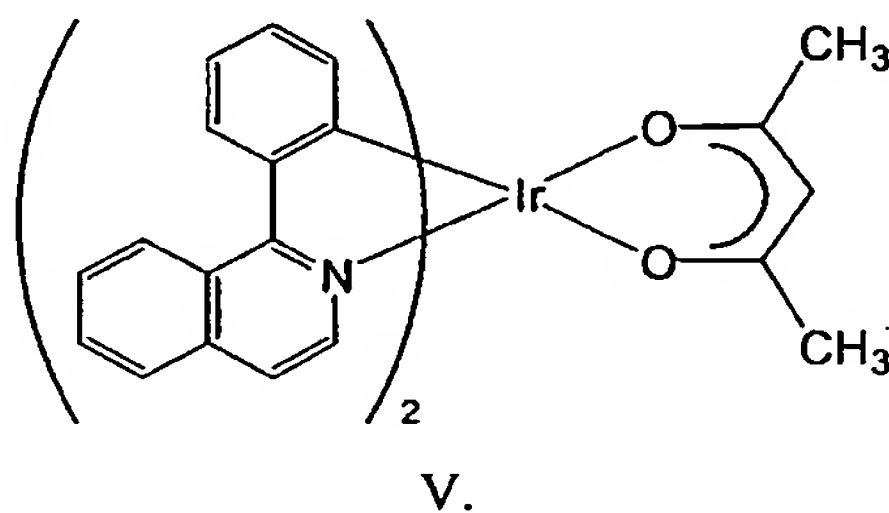


wherein:

- 15 R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
20 R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H; or
 R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H; or
 R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H; or
25 R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

In some such embodiments, R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H. In other such embodiments, R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H. In other such embodiments, R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H. In other such embodiments, R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H. In other such
 5 embodiments, R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H. In other such embodiments, R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H. In other such embodiments, R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H. In other such embodiments, R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H. In other such embodiments, R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H. In other such embodiments, R^9 is CH_3 ; and R^2 , R^3 , R^4 , and
 10 R^{10} are each H. In other such embodiments, R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

The present invention further includes organic light emitting devices comprising compounds of Formula V



15 The present invention further provides methods of increasing the wavelength of an electroluminescence maximum of an organic light emitting device comprising one or more compounds of the present invention, said methods comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is an activating group that influences the HOMO energy level of said
 20 compound, or at least one of said substituents is a deactivating group that influences the LUMO energy level of said compound.

The present invention further provides methods of decreasing the wavelength of an electroluminescence maximum of an organic light emitting device comprising one or more compounds of the present invention, said methods comprising choosing
 25 substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is a deactivating group that influences the HOMO energy level of said

compound, or at least one of said substituents is an activating group that influences the LUMO energy level of said compound.

The present invention also provides pixels comprising devices of the present invention.

5 The present invention also provides electronic displays comprising devices of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows structures of compounds 1 to 6.

10 Figure 2 shows structures of compounds 7 to 13.

Figure 3 shows a schematic for preparing compounds of the present invention.

Figure 4 shows a schematic for preparing compounds of the present invention.

Figure 5 shows structures of some bidentate ligands.

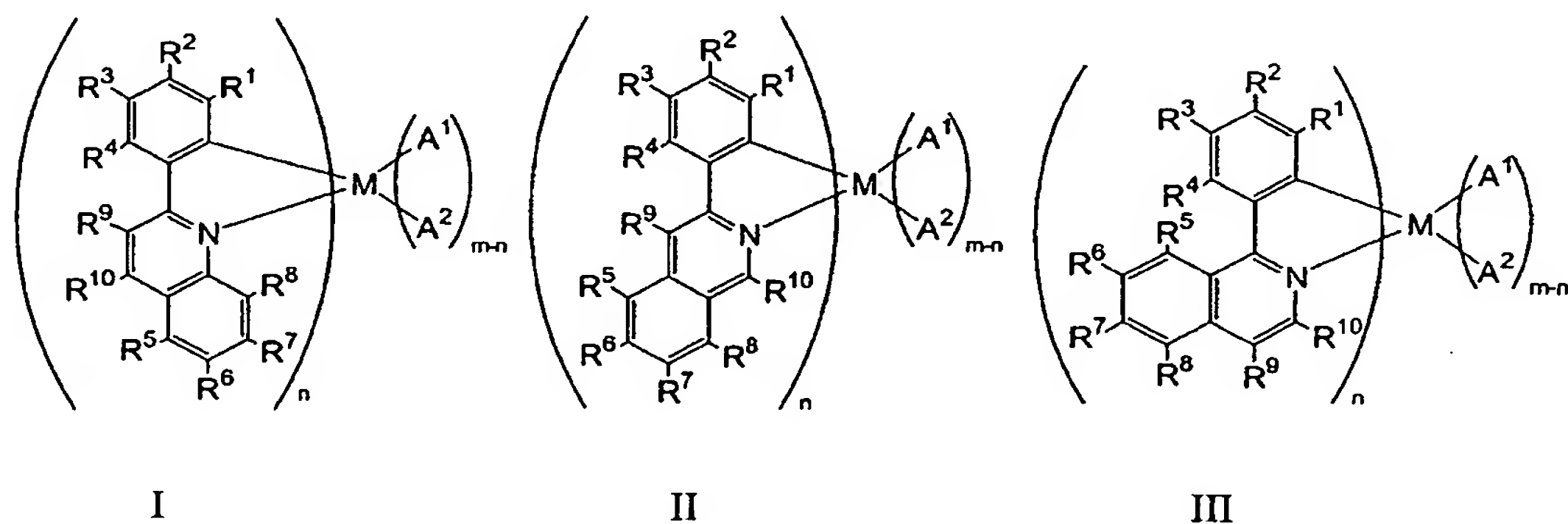
Figure 6 shows structures of further bidentate ligands.

15 Figure 7 illustrates the HOMO calculated for bis(phenylquinolinato)iridium(III) acetylacetonate compounds.

Figure 8 illustrates the LUMO calculated for bis(phenylquinolinato)iridium(III) acetylacetonate compounds.

20 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention includes, *inter alia*, compounds of Formulas I, II, and III



25 wherein:

M is a metal atom;

each A^1 and A^2 is, independently, a monodentate ligand; or A^1 and A^2 are covalently joined together to form a bidentate ligand;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9$, and R^{10} is, independently, H, F, Cl, Br, I, R^{11} , OR^{11} , $N(R^{11})_2$, $P(R^{11})_2$, $P(OR^{11})_2$, POR^{11} , PO_2R^{11} , PO_3R^{11} , SR^{11} , $Si(R^{11})_3$, $B(R^{11})_2$, $B(OR^{11})_2$, $C(O)R^{11}$, $C(O)OR^{11}$, $C(O)N(R^{11})_2$, CN, NO_2 , SO_2 , SOR^{11} , SO_2R^{11} , SO_3R^{11} ; and additionally, or alternatively, any one or more of R^1 and R^2 , or R^2 and R^3 , or R^3 and R^4 , or R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 , or R^9 and R^{10} , together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each R^{11} is, independently, H, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, C_3 - C_{40} heteroaryl; wherein R^{11} is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R^{12} , OR^{12} , $N(R^{12})_2$, $P(R^{12})_2$, $P(OR^{12})_2$, POR^{12} , PO_2R^{12} , PO_3R^{12} , SR^{12} , $Si(R^{12})_3$, $B(R^{12})_2$, $B(OR^{12})_2$, $C(O)R^{12}$, $C(O)OR^{12}$, $C(O)N(R^{12})_2$, CN, NO_2 , SO_2 , SOR^{12} , SO_2R^{12} , or SO_3R^{12} ;

each R^{12} is, independently, H, C_1 - C_{20} alkyl, C_1 - C_{20} perhaloalkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, or C_3 - C_{40} heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

wherein at least one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9$, and R^{10} is not H in compounds of Formula I. It is intended that the present compounds include any combination of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}$ substituents and fused cyclic groups.

According to compounds of the present invention, M can be any metal atom, including transition metals, lanthanides, actinides, main group metals, alkali metals and alkaline earth metals. Heavy metals provide thermal stability and superior phosphorescent properties to the present compounds and can include second and third row transition metals, lanthanides, actinides, as well as main group metals having atomic numbers greater than about 18. Second row transition metals include any of Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd, and third row transition metals include any of La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg. Main group metals having atomic numbers greater than 18 include Ga, Ge, In, Sn, Sb, Tl, Pb, Bi, and Po. In some embodiments, M is Ir, Os, Pt, Pb, Re, or Ru. In other embodiments, the metal atom is Ir. The metal atom M can have any formal charge designated as m. In some embodiments, the formal charge is positive such as 1+, 2+, 3+, 4+, 5+, 6+, 7+, or 8+. In further embodiments, formal charge is

greater than 1+, in other embodiments, formal charge is greater than 2+, and in yet further embodiments, formal charge can be 3+.

Monodentate ligands A^1 and A^2 can include any ligand capable of coordinating to a metal atom through one atom. Numerous monodentate ligands are known to those skilled in the art and many suitable examples are provided in Cotton and Wilkinson, *Advanced Inorganic Chemistry*, Fourth Ed., John Wiley & Sons, New York, 1980, which is incorporated herein by reference in its entirety. In some embodiments, monodentate ligands can include F, Cl, Br, I, CO, CN, $CN(R^{11})$, SR^{11} , SCN, OCN, $P(R^{11})_3$, $P(OR^{11})_3$, $N(R^{11})_3$, NO, N_3 , or a nitrogen-containing heterocycle optionally substituted by one or more substituents X. The phrase "nitrogen-containing heterocycle," as used herein refers to any heterocyclic group containing at least one nitrogen atom. Nitrogen-containing heterocycles can be saturated or unsaturated and include pyridine, imidazole, pyrrolidine, piperidine, morpholine, pyrimidine, pyrazine, pyridazine, pyrrole, 1,3,4-triazole, tetrazole, isoxazole, thiazole, derivatives thereof and the like. In further embodiments, one of A^1 and A^2 is a neutral monodentate ligand and the other of A^1 and A^2 is monoanionic, i.e., A^1 and A^2 have a combined charge of (-1). For example, A^1 can be chloro and A^2 can be pyridyl.

Together, A^1 and A^2 can also represent a bidentate ligand. Numerous bidentate ligands are known to those skilled in the art and many suitable examples are provided in Cotton and Wilkinson, *Advanced Inorganic Chemistry*, Fourth Ed., John Wiley & Sons, New York, 1980, which is incorporated herein by reference in its entirety. In some embodiments, bidentate ligands are monoanionic. Suitable bidentate ligands include acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, 8-hydroxyquinolate; amino acids, salicylaldehydes, and iminoacetonates. Structure of some suitable bidentate ligands are provided in Figure 5. Bidentate ligands can also include biaryl compounds. In some embodiments, the biaryl compounds coordinate to the metal atom through a carbon atom and a nitrogen atom. As used herein, the term "biaryl" refers to compounds comprising two aryl groups covalently joined by a single bond. The aryl groups of a biaryl compound can be aryl or heteroaryl, including both monocyclic or poly-cyclic aryl and heteroaryl groups. Examples of some biaryl groups are biphenyl, bipyridyl, phenylpyridyl, derivatives thereof and the like. Biaryl compounds can serve as bidentate ligands in metal coordination complexes, for instance, by coordinating through one atom in each of the two aryl groups. The coordinating atoms

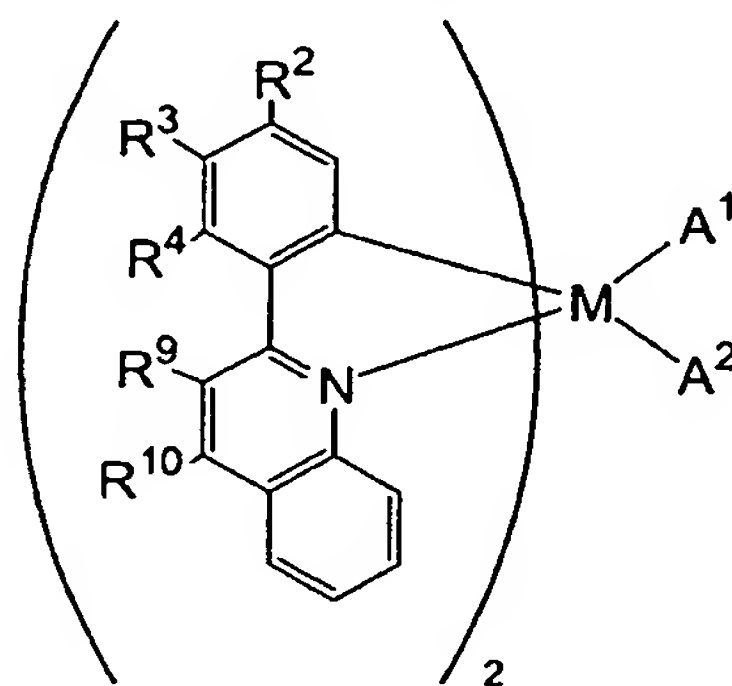
can be carbon or a heteroatom. Some further suitable bidentate ligands can include 2-(1-naphthyl)benzoxazole)), 2-phenylbenzoxazole, 2-phenylbenzothiazole, coumarin, thienylpyridine, phenylpyridine, benzothienylpyridine, 3-methoxy-2-phenylpyridine, thienylpyridine, tolylpyridine, phenylimines, vinylpyridines, arylquinolines, pyridyl-naphthalenes, pyridylpyrroles, pyridylimidazoles, phenylindoles, derivatives thereof and the like. Further suitable bidentate ligands are provided in Figure 6 (wherein Z is O, S, or NR; R is R¹¹; and n represents the number of substituents R ranging from, for example, 0 to 5) and in U.S. Ser. Nos. 09/274,609; 09/311,126; 09/452,346; 09/637,766; 60/283,814; and U.S. Ser. No. _____, filed October 16, 2001, entitled “Organometallic Compounds and Emission-Shifting Organic Electrophosphorescence” to Lamansky, *et al.*, each of which is incorporated herein by reference in its entirety.

Compounds of the present invention comprise at least one bidentate phenylquinolinato (pq) ligand. The term phenylquinolinato, or pq, is meant to refer to both substituted and non-substituted ligands, and the number (n) of coordinated pq ligands can be 1, 2, or 3. According to some embodiments, compounds of the present invention comprise m-1 pq ligands or, in some embodiments, two pq ligands. Phenylquinolinato ligands can be substituted with substituents R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ as defined above. Any combination of substituents is suitable. Substituents attached to adjacent carbon atoms of the pq ligands can, together, comprise a 4- to 7-member cyclic group that is fused to a ring of the ligand. For example, any or one or more of the pairs R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and R¹⁰ can comprise a fused cyclic group. The phrase “fused cyclic group” refers to a cyclic group that shares one or more bonds with a further cyclic group. Phenylquinolinato ligands of compounds of the present invention can have any number of fused cyclic group substituents, including 0, 1, 2, 3, 4, or 5 fused cyclic groups. Any feasible combination of fused cyclic groups and the remaining of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ that are not involved in a fused cyclic group are embodied by the present invention. In some embodiments of the present invention, at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is not H for compounds of Formula I. In some embodiments of the present invention, at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is not H for compounds of Formula II. In some embodiments of the present invention, at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is not H for compounds of Formula III. In further embodiments, any of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸,

R^9 , and R^{10} can be H, methyl (CH_3), trifluoromethyl (CF_3), methoxy (OCH_3), or fluoro (F), and in other embodiments, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is CH_3 , CF_3 , OCH_3 , or F. Additionally, any of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} can be H, an activating group, or a deactivating group. In yet further embodiments, at least one of R^3 , R^4 , R^9 , and R^{10} is a substituent other than H.

The present invention further includes compounds of Formula I where M, A^1 , A^2 , m, and n are as hereinbefore defined and each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is, independently, H, an activating group, or a deactivating group; and additionally, or alternatively, any one or more of R^1 and R^2 , or R^2 and R^3 , or R^3 and R^4 , or R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 , or R^9 and R^{10} , together form, independently, a fused 4- to 7-member cyclic group, wherein the cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the cyclic group is optionally substituted by one or more substituents X; and wherein at least one of R^3 , R^9 , and R^{10} is an activating group or a deactivating group, or wherein at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group.

The present invention further includes compounds of Formula VI

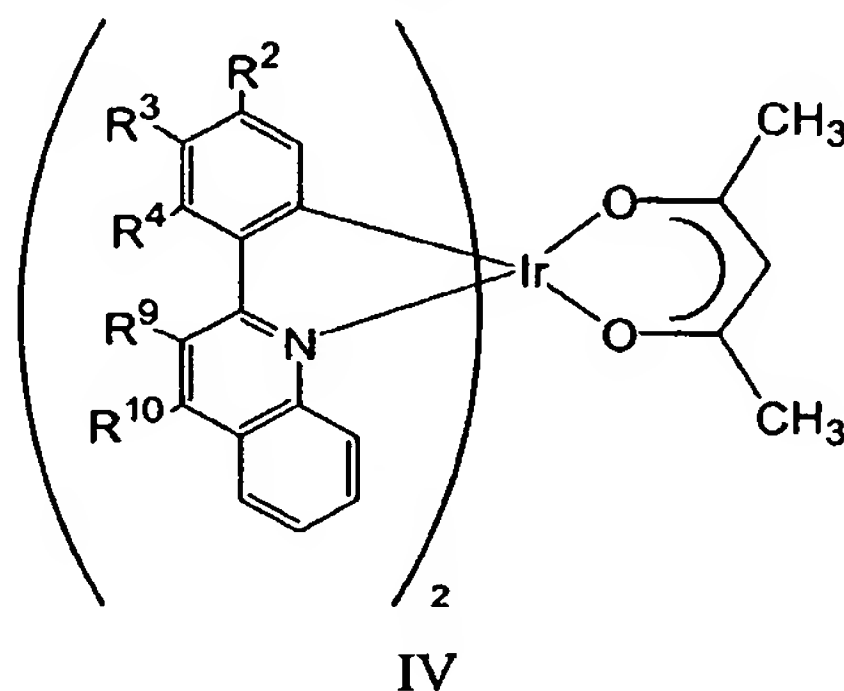


VI

wherein M, A^1 , A^2 , are as hereinbefore defined. According to Formula VI, R^4 can be F and R^2 , R^3 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^4 can be OCH_3 and R^2 , R^3 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^3 is OCH_3 and R^2 , R^4 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^2 can be OCH_3 and R^3 , R^4 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^4 can be CF_3 ; and R^2 , R^3 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^3 can be CF_3 and R^2 , R^4 , R^9 , and R^{10} can each, independently, be H, an activating group or deactivating group; or R^2 can be

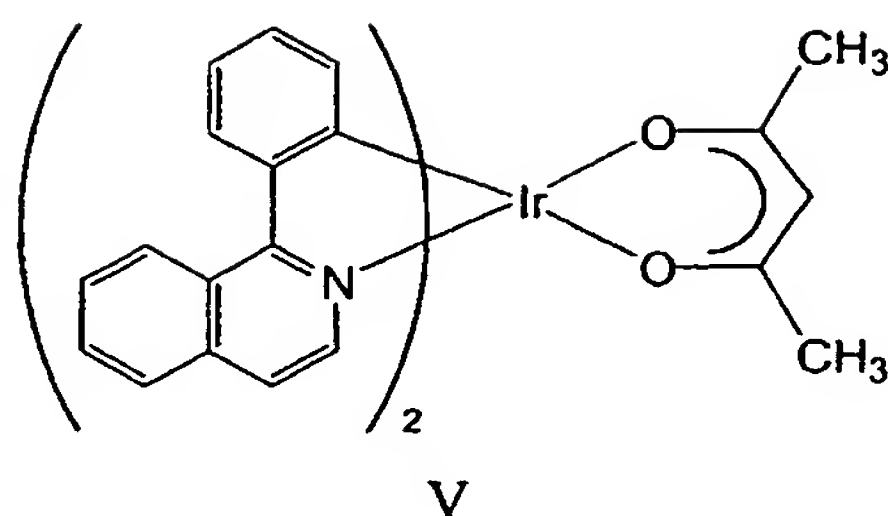
CF₃ and R³, R⁴, R⁹, and R¹⁰ can each, independently, be H, an activating group or deactivating group; or R² and R⁴ can each be F and R³, R⁹, and R¹⁰ can each, independently, be H, an activating group or deactivating group; or R⁹ can be CH₃ and R², R³, R⁴, and R¹⁰ can each be, independently, H, an activating group or deactivating group;
 5 or R¹⁰ is CH₃; and R², R³, R⁴, and R⁹ can each, independently, be H, an activating group or deactivating group.

The present invention further includes compounds of Formula IV.



10 According to Formula IV, compounds of the present invention include those where R⁴ is F; and R², R³, R⁹, and R¹⁰ are each H (compound 2); or R⁴ is OCH₃; and R², R³, R⁹, and R¹⁰ are each H (compound 4); or R³ is OCH₃; and R², R⁴, R⁹, and R¹⁰ are each H (compound 5); or R² is OCH₃; and R³, R⁴, R⁹, and R¹⁰ are each H (compound 6); or R⁴ is CF₃; and R², R³, R⁹, and R¹⁰ are each H (compound 7); or R³ is CF₃; and R², R⁴, R⁹, and R¹⁰ are each H (compound 8); or R² is CF₃; and R³, R⁴, R⁹, and R¹⁰ are each H (compound 9); or R² and R⁴ are each F; and R³, R⁹, and R¹⁰ are each H (compound 10); or R⁴ and R¹⁰ are each CH₃; and R², R³, and R⁹ are each H; or R⁹ is CH₃; and R², R³, R⁴, and R¹⁰ are each H (compound 11); or R¹⁰ is CH₃; and R², R³, R⁴, and R⁹ are each H (compound 12). Structures of some of these compounds and others are provided in
 20 Figures 1 and 2.

Also embodied by the present invention is a compound of Formula V (compound 13).



Activating and deactivating groups are well recognized by those skilled in the art,
5 and/or can be readily identified by routine measurements. As is well understood
according to theory, activating and deactivating groups are so named for their respective
abilities to stabilize or destabilize the arenium ion intermediate state in electrophilic
substitution reactions of aromatic compounds and to direct orientation (i.e., ortho-para
vs. meta directors). The activating or deactivating ability of a particular substituent is
10 governed by several factors including the inductive effect and resonance effect. Not
wishing to be bound by any particular theory, it is believed that the inductive effect
arises from the electrostatic interaction of the substituent with the molecule to which the
substituent is attached. For example, if the substituent is more electronegative than the
atom to which it is attached, the substituent inductively draws electron density away
15 from the molecule. Substituents having higher electronegativity have stronger inductive
effects. Substituents bearing a full or partial charge also tend to withdraw electron
density inductively. On the other hand, the resonance effect relates to the contribution of
a substituent to resonance stabilization of a molecule. For example, it is believed that a
substituent having a lone pair of electrons can contribute to further resonance structures
20 by delocalization of the lone pair onto an aromatic molecule.

Varying contributions of inductive and resonance effects help determine the
activating or deactivating abilities of a substituent. A substituent that is deactivating
tends to destabilize the arenium ion intermediate of electrophilic substitution by
withdrawing electron density from the molecule such as through the inductive effect.
25 Thus, strongly electronegative substituents, such as halogens, can be considered
deactivating since destabilizing inductive effects can dominate over stabilizing
resonance effects. Weaker electronegative substituents, such as hydroxyl or methoxy,
can be considered activating since resonance effects involving the oxygen lone pair tend
to dominate over deactivating inductive effects. Although alkyl groups lack a lone pair

to contribute to resonance stabilization, they are typically considered activating groups due to hyperconjugation.

Some suitable activating groups include, for example, alkyl, heteroalkyl, aryl, heteroaryl, alkoxy, aryloxy, hydroxy, mercapto, thiolato, amino, phosphino, alkylcarbonylamino, arylcarbonylamino, and the like. As an example, methyl and methoxy can serve as activating groups. Some suitable activating groups have a lone pair of electrons (e.g., alkoxy, amino, etc.) Some suitable deactivating groups include, for example, halo, cyano, nitro, aldehyde, alkylcarbonyl, arylcarbonyl, ammonium, perhaloalkyl, carboxylic acid, alkoxycarbonyl, aryloxycarbonyl, sulfo (SO₃H), and the like. As an example, fluoro and trifluoromethyl can serve as deactivating groups. Activating and deactivating groups are treated in detail, for example, in T.W. Graham Solomons, *Organic Chemistry*, Fifth ed., pp. 654-661 (1992), which is incorporated herein by reference in its entirety.

As used herein, the term "alkyl" includes linear, branched, and cyclic alkyl groups. In some embodiments, alkyl groups are C₁-C₂₀ alkyl groups. Examples of alkyl groups include, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, cyclohexyl, norbornyl, and the like. As used herein, the term "heteroalkyl" refers to alkyl groups including one or more heteroatoms such as O, S, or N. Heteroalkyl groups can also comprise unsaturations. Examples of heteroalkyl groups include pyrrolidinyl, piperidinyl, morpholinyl, and the like. The term "perhaloalkyl" refers to alkyl groups substituted by halogen. Examples of a perhaloalkyl group include trifluoromethyl, trichloromethyl, pentafluoroethyl, and the like. "Alkenyl" groups refer to alkyl groups having one or more double bonds, and "alkynyl" groups refer to alkyl groups having one or more triple bonds. "Alkoxy" groups can have from about 1 to about 20 carbon atoms and can include, for example, methoxy, ethoxy, propoxy, n-butoxy, isobutoxy, and the like. "Aryloxy" groups can have from about 3 to about 40 carbon atoms and can include, for example, phenoxy and the like. "Aryl" groups can be any mono- or polycyclic aromatic group, and "heteroaryl" refers to an aryl group including one or more heteroatoms such as O, S, or N. Aryl groups can have 3 to about 40 carbon atoms and can include, for example, phenyl, 4-methylphenyl, naphthyl, anthracenyl, phenanthryl, and the like. Heteroaryl groups can include, for example, pyridyl, indolyl, benzothiophene, quinolinyl, and the like. "Amino" groups, as used herein, include amino, alkylamino, dialkylamino, arylamino, and diarylamino groups. Examples of

amino groups include, NH_2 , methylamino, dimethylamino, phenylamino, diphenylamino, and the like. "Phosphino" groups, as used herein, include phosphino, alkylphosphino, dialkylphosphino, arylphosphino, and diarylphosphino. Some examples of phosphino groups include PH_2 , methylphosphino, dimethylphosphino, phenylphosphino, 5 diphenylphosphino, and the like. "Thiolato" groups can have from about 1 to about 20 carbon atoms and can include, for example, thiomethoxy, thiophenoxy, and the like. "Halo" groups include fluoro, chloro, bromo, and iodo, for instance.

The compounds of the present invention can be photoluminescent. In some embodiments, the present compounds are efficient phosphors, having, for example, a significant portion of luminescence arising from phosphorescent emission. The compounds can emit at any color, including red, green, blue, and other colors (i.e., red-orange, blue-green, etc.). In some embodiments, the emission can be red or reddish. Color of emission can be estimated from the photoluminescence spectrum. A luminescence maximum of from about 550 to about 700 nm can indicate red or reddish 15 emission. A maximum at lower wavelengths can indicate green or blue emission. Additionally, the color of emission for compounds of the present invention can be described by color index coordinates x and y (Commission Internationale de L'Eclairage (CIE) 1931 standard 2-degree observer; see, e.g., Shoustikov, *et al.*, *IEEE Journal of Selected Topics in Quantum Electronics*, 1998, 4, 3; Dartnall, *et al.*, *Proceedings of the Royal Society of London B*, 1983, 220, 115; Gupta, *et al.*, *Journal of Photochemistry*, 1985, 30, 173; *Colorimetry*, 2nd ed., Publication CIE 15.2-1986 (ISBN 3-900-734-00-3); and www.cie.co.at/cie/). For example, a compound emitting in the reds can have coordinates of from about 0.5 to about 0.8 for x and 0.2 to about 0.5 for y . Any set of color coordinates can be within reach of the compounds of the present invention. 20

Substitution of the phenylquinolinato ligand by various substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} , can affect emission color. In fact, emission color can be deliberately controlled, or "tuned," in compounds of the present invention by judicious selection of substituents. Since emission color is sensitive to the energy gap between the HOMO and LUMO energy levels of the compound, substituents that predictably affect 25 either or both of these molecular orbitals can be purposefully incorporated into compounds of the present invention to achieve a certain color. For example, molecular orbital (MO) calculations can help indicate which carbon atoms of the phenyl and quinolinyl moieties of the ligand contribute to the HOMO or LUMO. Results from an 30

example MO calculation for a bis(phenylquinolinato ligand) complex are shown in Figures 7 and 8. Figure 7 shows the ligand atoms, which are predominantly on the phenyl moiety, that are involved in the HOMO. Figure 8 shows the ligand atoms, which are predominantly on the quinolinyl moiety, that are involved in the LUMO.

5 Substituents attached to atoms of the ligand involving the HOMO influence the HOMO by either stabilizing (lowering its energy) or destabilizing it (raising its energy). Accordingly, substituents that are activating, and attached to a carbon atom contributing to the HOMO, can raise the HOMO energy level, thereby decreasing the HOMO-LUMO gap and increasing the wavelength of emission (red-shift, bathochromic shift). Similarly,

10 substituents that are deactivating (largely electron-withdrawing) can lower the HOMO energy level, thereby increasing the HOMO-LUMO gap and decreasing the wavelength of emission (blue-shift, hypsochromic shift). Conversely, substituents that are activating, and attached to a carbon atom contributing to the LUMO, can raise the LUMO energy level, thereby increasing the HOMO-LUMO gap and decreasing the wavelength of

15 emission. Similarly, substituents that are deactivating, and attached to a carbon atom contributing to the LUMO, can lower the LUMO energy level, thereby decreasing the HOMO-LUMO gap and increasing the wavelength of emission. In addition, deactivating groups can be substituted on ligand atoms that are not involved in either the HOMO or LUMO (i.e., nodes) generally resulting in blue-shifted emission color.

20 As is evident, emission color can be deliberately red-shifted or blue-shifted upon selection of ligand and substitution site in order to obtain a desired hue. Accordingly, the present invention encompasses methods of increasing the wavelength of emission, such as can be measured by a photoluminescence maximum for a compound of the present invention (or electroluminescence maximum for a device comprising a compound of the

25 present invention), relative to emission from a reference compound having the same structure, but having hydrogen(s) at the substitution site(s). In some embodiments, the methods comprise choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of these is an activating group that influences the HOMO energy level of the compound. Alternatively, or in addition, at least one of the substituents can be a

30 deactivating group that influences the LUMO energy level of said compound. Example 2, *infra*, details results from a representative method of the invention. Similarly, the present invention further includes methods of decreasing the wavelength of emission, such as can be measured by a photoluminescence maximum for a compound of the

present invention (or electroluminescence maximum for a device comprising a compound of the present invention), relative to emission from a reference compound having the same structure, but having hydrogen(s) at the substitution site(s). In some embodiments, the method comprises choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of these substituents is a deactivating group that influences the HOMO energy level of the compound. Alternatively, or in addition, at least one of the substituents can be an activating group that influences the LUMO energy level of the compound.

In some embodiments, the methods of increasing emission wavelength can comprise selection of substituents such that R^3 is an activating group. Conversely, choosing R^3 as a deactivating group can relate to methods according to the present invention for decreasing emission wavelength. In other embodiments, methods for increasing emission wavelength can comprise choosing R^{10} as a deactivating group. Similarly, methods for decreasing emission wavelength can comprise choosing R^{10} as an activating group.

Processes for preparing compounds described herein are also embodied by the present invention. A synthesis schematic for compounds of Formula I is shown in Figure 3. A synthesis schematic for compounds of Formula II is shown in Figure 4. Compounds of Formula III can be made similarly. Phenylquinolinato ligands (L) having desired substitution according to the present invention can be made using the general procedure of coupling phenyl boronic acid having desired substitution with chloroquinoline (e.g., 2-chloroquinoline, 3-chloroisoquinoline, or 2-chloroisoquinoline) also having desired substitution. Coupling procedures can be, for example, conducted under Suzuki conditions in the presence of palladium(II) (see, e.g., Miyaura, *et al.*, *Chem. Rev.* 1995, 2457). The quinoline (or isoquinoline) and boronic acid starting materials can be obtained from commercial sources or synthesized by methods known in the art. For example, 3-chloroisoquinoline can be made according to the procedures described in Haworth, R. D., *et al.*, *J. Chem. Soc.*, 1948, 777.

Phenylquinoline ligands (L) having desired substitution can be coordinated to a metal atom by, for example, contacting the ligands with a metal halide complex. Metal halide complexes include compounds comprising at least one metal coordinated to one or more halide ligands. Metal halide complexes can be of the Formula $M(Q)_q$ where Q is a halide ligand and q is the number of halide ligands. For example, q can range from about

2 to about 6. For the preparation of iridium-containing compounds, the metal halide complex can be IrCl_3 . This and other metal halide complexes are well known in the art and commercially available. Under sufficient time and conditions, the contacting can result in the formation of a metal-containing intermediate, having mixed coordination of halide and phenylquinoline ligands L. In some embodiments, the metal atom of the intermediate can coordinate to at least one L. In other embodiments, the metal atom of the intermediate can coordinate two L. In further embodiments, the intermediate can be polynuclear, comprising, for example, more than one metal atom and bridging halide ligands. When the metal halide complex is IrCl_3 , the metal-containing intermediate can be an iridium dimer complex, having, for example, the structure $\text{L}_2\text{Ir}(\mu\text{-Cl})_2\text{IrL}_2$. Any remaining halide ligands of the intermediate, including bridging halides, can be replaced by ligand substitution with one or more ancillary ligands, such as represented by A^1 and A^2 in any of the Formulas I to IV, to yield compounds of the present invention. A^1 and A^2 can be monodentate ligands or are combined to form a single bidentate ligand. For example, 2,4-pentanedione in the presence of base can replace coordinated halide ligands in the metal-containing intermediate to give acetylacetonato complexes of the present invention. Syntheses of exemplary compounds of the present invention are provided in Examples 3-15.

The compounds described herein can be used as emitters in organic light emitting devices. Accordingly, the compounds can be present in an emissive layer (i.e., a layer from which light is primarily emitted) of a such device. The emissive layer can be, for example, a layer consisting essentially of one or more compounds of the present invention. The present compounds can also be present as dopants. For example, an emissive layer can comprise host material doped with one or more of the present compounds. The host material can comprise any compound, including organic and organometallic compounds, suitable in an emissive layer in an OLED. For example, organic host material can comprise BCP (bathocuproine or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), CBP (4,4'-N,N'-dicarbazole biphenyl), OXD7 (1,3-bis(N,N-*t*-butylphenyl)-1,3,4-oxadiazole), TAZ (3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole), NPD (4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl), and the like. Other host material can comprise CuPc (copper phthalocyanine), Alq₃ (aluminum tris(8-hydroxyquinolate)), BALq ((1,1'-biphenyl)-4-olato)bis(2-methyl-8-quinolinolato N1,O8)aluminum), and the like. Other materials that can be included in an emissive

layer, in addition to the compounds of the present invention, include Irppy (tris(2-phenylpyridinato-N,C2')iridium(III)), FIrpic (bis(2-(4,6-difluorophenyl)pyridinato-N,C2')iridium(III)(picolinate)), and other metal complexes such as those described in U.S. Ser. Nos. 09/274,609; 09/311,126; 09/452,346; 09/637,766; 60/283,814; and U.S. Ser. No. _____, filed October 16, 2001, entitled "Organometallic Compounds and Emission-Shifting Organic Electrophosphorescence" to Lamansky, *et al.*, each of which is incorporated herein by reference in its entirety. As dopants, the present compounds can be present in the emissive layer, such as in host material, in amounts of from about 1 to about 20 wt%, about 5 to about 15 wt%, about 5 to about 10 wt%, or other similar ranges.

Accordingly, the present invention includes compositions comprising compounds of the present invention. In some embodiments, compositions comprise at least one compound of the present inventions and a further compound suitable for use in an OLED. For example, further compounds can include any of the host materials mentioned above. Additionally, further compounds can include other emitters or metal complexes, such as FIrpic, Irppy, and other complexes mentioned above and incorporated by reference.

Devices comprising the present compounds have superior properties as compared with known devices. For example, high external quantum and luminous efficiencies can be achieved in the present devices. Device lifetimes are also generally better than, or at least comparable to, some of the most stable fluorescent devices reported. Data for some devices according to the present invention are provided in Example 1.

Devices of the present invention can emit at any color. Some devices of the present invention, such as, for example, those comprising iridium, can be red emitters. Red devices of the invention can have electroluminescence maxima of from about 550 to about 700 nm. Similarly, color index coordinates (CIE) for red devices of the invention can range from about 0.5 to about 0.8 for *x* and about 0.2 to about 0.5 for *y*. In some embodiments, devices, such as, for example, red devices, can have external quantum efficiencies greater than about 4%, 5%, 6%, 7%, 8%, 10%, 12%, or higher at a brightness greater than about 10, 100, 1000 cd/m², or more.

Typical devices are structured so that one or more layers are sandwiched between a hole injecting anode layer and an electron injecting cathode layer. The sandwiched layers have two sides, one facing the anode and the other facing the cathode. Layers are

generally deposited on a substrate, such as glass, on which either the anode layer or the cathode layer may reside. In some embodiments, the anode layer is in contact with the substrate. In some embodiments, for example when the substrate comprises a conductive or semi-conductive material, an insulating material can be inserted between the electrode
5 layer and the substrate. Typical substrate materials, that may be rigid, flexible, transparent, or opaque, include glass, polymers, quartz, sapphire, and the like.

In some embodiments, devices of the present invention comprise further layers in addition to a layer comprising the present compounds (*e.g.*, an emissive layer). For example, in addition to the electrodes, devices can include any one or more hole
10 blocking layers, electron blocking layers, exciton blocking layers, hole transporting layers, electron transporting layers, hole injection layers, or electron injection layers. Anodes can comprise an oxide material such as indium-tin oxide (ITO), Zn-In-SnO₂, SbO₂, or the like, and cathodes can comprises a metal layer such as Mg, Mg:Ag, or LiF:Al. Among other materials, the hole transporting layer (HTL) can comprise triaryl
15 amines or metal complexes such as those described in U.S. Ser. Nos. 60/317,540 and 60/317,540, each of which is incorporated herein by reference in its entirety. Similarly, the electron transporting layer (ETL) can comprise, for example, aluminum tris(8-hydroxyquinolate) (Alq₃) or other suitable materials. Additionally, a hole injection layer can comprise, for example, 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine
20 (MTDATA) or polymeric material such as poly(3,4-ethylenedioxythiophene) (PEDOT), or metal complex such as, for example, copper phthalocyanine (CuPc), or other suitable materials. Hole blocking, electron blocking, and exciton blocking layers can comprise, for example, BCP, BAq, and other suitable materials such as Flrpic or other metal complexes described in U.S. Ser. Nos. 60/317,540 and 60/317,540, each of which is
25 incorporated herein by reference in its entirety. Compounds of the present invention can also be included in any of the above mentioned layers.

Light emitting devices of the present invention can be fabricated by a variety of techniques well known to those skilled in the art. Small molecule layers, including those comprised of neutral metal complexes, can be prepared by vacuum deposition, organic
30 vapor phase deposition (OVPD), such as disclosed in U.S. Ser. No. 08/972,156, filed November 17, 1997, which is incorporated herein by reference in its entirety, or solution processing such as spin coating. Polymeric films can be deposited by spin coating and chemical vapor deposition (CVD). Layers of charged compounds, such as

salts of charged metal complexes, can be prepared by solution methods such a spin coating or by an OVPD method such as disclosed in U.S. Pat. No. 5,554,220, which is incorporated herein by reference in its entirety. Layer deposition generally, although not necessarily, proceeds in the direction of the anode to the cathode, and the anode typically rests on a substrate. Devices and techniques for their fabrication are described throughout the literature and in, for example, U.S. Pat. Nos. 5,703,436; 5,986,401; 6,013,982; 6,097,147; and 6,166,489, each of which is incorporated herein by reference in its entirety. For devices from which light emission is directed substantially out of the bottom of the device (i.e., substrate side), a transparent anode material such as ITO may be used as the bottom electron. Since the top electrode of such a device does not need to be transparent, such a top electrode, which is typically a cathode, may be comprised of a thick and reflective metal layer having a high electrical conductivity. In contrast, for transparent or top-emitting devices, a transparent cathode may be used such as disclosed in U.S. Pat. Nos. 5,703,436 and 5,707,745, each of which is incorporated herein by reference in its entirety. Top-emitting devices may have an opaque and/or reflective substrate, such that light is produced substantially out of the top of the device. Devices can also be fully transparent, emitting from both top and bottom.

Transparent cathodes, such as those used in top-emitting devices preferably have optical transmission characteristics such that the device has an optical transmission of at least about 50%, although lower optical transmissions can be used. In some embodiments, devices include transparent cathodes having optical characteristics that permit the devices to have optical transmissions of at least about 70%, 85%, or more. Transparent cathodes, such as those described in U.S. Pat. Nos. 5,703,436 and 5,707,745, typically comprise a thin layer of metal such as Mg:Ag with a thickness, for example, that is less than about 100 Å. The Mg:Ag layer can be coated with a transparent, electrically-conductive, sputter-deposited, ITO layer. Such cathodes are often referred to as compound cathodes or as TOLED (transparent-OLED) cathodes. The thickness of the Mg:Ag and ITO layers in compound cathodes may each be adjusted to produce the desired combination of both high optical transmission and high electrical conductivity, for example, an electrical conductivity as reflected by an overall cathode resistivity of about 30 to 100 ohms per square. However, even though such a relatively low resistivity can be acceptable for certain types of applications, such a resistivity can still be somewhat too high for passive matrix array OLED pixels in which the current that

powers each pixel needs to be conducted across the entire array through the narrow strips of the compound cathode.

Light emitting devices of the present invention can be used in a pixel for an electronic display. Virtually any type of electronic display can incorporate the present devices. Displays can include computer monitors, televisions, personal digital assistants, printers, instrument panels, bill boards, and the like. In particular, the present devices can be used in flat panel displays and heads-up displays.

The following examples illustrate the invention and are not intended to limit the same. Those skilled in the art will recognize, or be able to ascertain through routine experimentation, numerous equivalents to the specific substances and procedures described herein. Such equivalents are considered to be within the scope of the present invention.

EXAMPLES

Example 1: Compound and device properties.

Substituted phenylquinolinato iridium(III) acetylacetonate compounds 2 to 13 and comparative compound 1 (see Figures 1 and 2) were characterized and used as emissive dopants in organic light emitting devices having the structure glass/ITO/CuPc/NPD/CPB:dopant/BAIq/Alq₃/LiF/Al. Photophysical properties of the compounds and devices were surprisingly remarkable as illustrated in Table I. Device emissions ranged from orange to deep red. The highest efficiency was obtained from an orange-red device comprising compound 11. External quantum efficiencies greater than 8% and luminous efficiencies higher than 20 cd/A were routinely obtained at the brightness level of a full color display, i.e., 10-1000 cd/m². These efficiencies are almost an order of magnitude higher than for known red-emitting fluorescent devices such as the DCJTB devices reported in Hatwar, *et al.*, *Proceedings of the 10th International Workshop of Inorganic and Organic Electroluminescence*, December, 2000, Hamamatsu, Japan, p. 31. Lifetime studies under constant current drive showed half-lives extrapolated to longer than 5,000 hours at initial brightness of 300 cd/m².

Table 1

No.	CIE (x, y) in CH ₂ Cl ₂	CIE (x, y) in device	External Quantum Efficiency @10 mA/cm ²	Brightness Cd/A @10mA/cm ²	Power Efficiency Lm/W @10mA/cm ²	Photo- luminescence maximum (nm)
1	(0.62, 0.38)	(0.62, 0.38)	10.3	17.4	4.8	606 nm
2	(0.60, 0.40)	(0.58, 0.40)	6.8	13.2	3.9	602 nm
3	(0.65, 0.35)	(0.65, 0.34)	6.4	6.8	2.0	626 nm
4	(0.61, 0.39)	(0.61, 0.38)	8.3	14	3.9	608 nm
5	(0.70, 0.30)	(0.70, 0.30)	5.8	2.0	0.53	656 nm
6	(0.58, 0.42)	(0.58, 0.42)	8.4	17.3	4.6	591 nm
7	(0.65, 0.35)	(0.58, 0.40)	3.0	4.4	1.3	632 nm
8	(0.56, 0.44)	(0.54, 0.45)	4.9	11.4	3.3	590 nm
9	(0.59, 0.41)	(0.56, 0.42)	5.1	10.4	3.0	592 nm
10	(0.55, 0.45)	(0.54, 0.46)	6.6	16.8	4.7	585 nm
11	(0.59, 0.41)	(0.60, 0.40)	11.8	22.9	6.8	598 nm
12	(0.65, 0.35)	(0.65, 0.35)	9.8	11	3.2	626 nm
13	(0.68, 0.32)	(0.67, 0.33)	10.5	8.1	2.4	626 nm

Example 2: Tuning emission color.

- 5 By attaching an activating substituent to a ligand atom involved in the HOMO of a compound of the present invention, a 50 nm red-shift in the photoluminescence maximum was observed relative to an unsubstituted reference compound. For example, the photoluminescence maximum for compound 5 (see Figure 1) is reported as 656 nm in Table 1. This is a 50 nm increase relative to reference compound 1 (see Figure 1),
- 10 having a photoluminescence maximum at 606 nm (Table 1). MO calculations predicted that the R³ substituent contributes to the HOMO (see Figure 7). Indeed, substitution at R³ with activating methoxy results in a distinct red-shift in the photoluminescence spectrum as compared with the reference compound 1 where R³ is hydrogen.

15 **Example 3: Synthesis of Bis(2-phenylquinoline)iridium(III) acetylacetonate (Compound 1)**

Step 1

- 20 2-Phenylquinoline (6.0 g, 29 mmol) and iridium(III) chloride hydrate (5.2 g, 14 mmol) were added to a flask containing 80 mL of 2-methoxyethanol and 20 mL of distilled water. The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the red precipitate formed was vacuum filtered and washed first with absolute ethanol followed by hexanes. The dichloro-bridged dimer was dried in a vacuum oven to give 6.7 g (38% yield). The product was not purified any further but used directly in the next step.

Step 2

The dichloro-bridged dimer (6.7 g, 5.3 mmol) was added to 200 mL of a solution containing 2-methoxyethanol (150 mL). Sodium carbonate (5.6 g, 53 mmol) and 2,4-pentanedione (5.3 g, 53 mmol) were added to the reaction mixture. The reaction mixture
5 was heated to 105 °C. and stirred under nitrogen for 18 hours. After the reaction was cooled to room temperature, the precipitate was vacuum filtered. The filtered product was added to 500 mL of distilled water and stirred for 10 minutes. The red precipitate was vacuum filtered, washed with additional distilled water, followed by several rinses with absolute ethanol followed by hexanes to give bis(2-phenylquinoline)iridium(III)
10 acetylacetonate (3.0 g). The desired product was purified by vacuum sublimation.

Example 4: Synthesis of Bis[2-(2-fluorophenyl)quinoline]iridium(III) acetylacetonate (Compound 2)

Step 1

15 2-Chloroquinoline (4.9 g, 30 mmol), 2-fluorophenylboronic acid (5.0 g, 36 mmol) and K₂CO₃ (12 g) were dissolved in the solvent mixture of 50 mL ethylene glycol dimethyl ether and 75 mL water. To the stirred solution was added 1.7 g tetrakis(triphenylphosphine)palladium(0) and the mixture refluxed under N₂ for 20 hours. The reaction mixture was cooled and the water extracted with methylene chloride
20 three times. The combined organic phase was washed with portions of brine. The organic layer was then dried with anhydrous sodium sulfate, filtered, and evaporated of solvent. The crude material was purified on a silica gel column to give 2-(2-fluorophenyl)quinoline (6.4 g, 96% yield).

Step 2

25 2-(2-Fluorophenyl)quinoline (6.2 g, 28 mmol) was dissolved in the solvent mixture of 90 mL 2-methoxyethanol and 30 mL of water. To the stirred solution was added 4.9 g iridium(III) chloride trihydrate. The mixture refluxed under N₂ overnight. The solution was cooled down and filtered. The reddish solid was washed with ethanol
30 twice and dried in vacuum to give 2-(2-fluorophenyl)quinoline Ir dimer (5.2 g).

Step 3

- 2-(2-Fluorophenyl)quinoline Ir dimer (5.2 g) was added to 90 mL 2-methoxyethanol and to the stirred solution was added 1.0 g 2,4-pentanedione and 4.2 g sodium carbonate. The mixture was heated at 100°C with stirring overnight under N₂.
- 5 The cooled mixture was then filtered to give bis[2-(2-fluorophenyl)quinoline]iridium(III) acetylacetonate (3.0 g) which was further purified by vacuum sublimation.

Example 5: Synthesis of Bis[2-(2-methylphenyl)quinoline]iridium(III) acetylacetonate (Compound 3)

10 *Step 1*

- To a 500 mL round bottom flask was added, 2-chloroquinoline (4.7 g, 31 mmol), *o*-tolylphenyl boronic acid (4.7g, 36 mmol) into 100 mL of ethylene glycol dimethyl ether. Sodium carbonate (8.9 g, 84 mmol) was dissolved into 50 mL of distilled water and added to the reaction mixture. After the addition of 0.1 mole % of
- 15 triphenylphosphine (0.8 g) followed by 0.025 mol% of palladium(II) acetate (0.2 g). the reaction was heated under a nitrogen atmosphere for 4 hours. After cooling, additional ethyl acetate was added and the aqueous layer discarded. The organic layer was washed with a saturated solution of brine. The organic layer was dried over magnesium sulfate, filtered and the solvent removed by a rotary evaporator. The crude yellow oil was
- 20 purified by column chromatography using a silica gel column and 20% ethyl acetate/hexanes as the eluants. The pure product was collected, combined and concentrated to give 2-(2-methylphenyl)quinoline (6.0 g, 75% yield).

Step 2

- 25 2-(2-Methylphenyl)quinoline (6.0 g, 27 mmol) and iridium(III) chloride trihydrate (5.2 g, 15 mmol) were added to a flask containing a solution of 2-ethoxyethanol (80 mL) and water (20 mL). The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 20 hours. After cooling the dark red precipitate that formed was filtered and washed with ethanol followed by hexanes to give
- 30 the dichloro-bridged dimer (6.4 g).

Step 3

The above dichloro-bridged dimer (2.7 g, 20 mmol) and 2,4-pentanedione (2.0 g, 20 mmol) were added to dichloromethane and a solution of potassium carbonate (5.5 g, 50 mL) and refluxed overnight. The reaction mixture was cooled and the solids removed
5 by vacuum filtration. The filtrate was concentrated and the crude product purified by a silica gel column using ethyl acetate and hexanes as the eluants to give bis[2-(2-methylphenyl)quinoline]iridium(III) acetylacetonate (1.5 g) which was further purified by sublimation.

10 **Example 6: Synthesis of Bis[2-(2-methoxyphenyl)quinoline]iridium(III) acetylacetonate (Compound 4)**

Step 1

2-Chloroquinoline (2.45 g, 15.0 mmol), *o*-methoxyphenylboronic acid (2.73 g, 18.0 mmol,) and potassium carbonate (5.59 g, 40.4 mmol) were dissolved in 40 mL
15 ethylene glycol dimethyl ether and 20 mL of water. To the stirred solution was added tetrakis(triphenylphosphine)palladium(0) (1.04 g, 0.89 mmol) and the entire mixture was allowed to reflux under a N₂ atmosphere for 20 hours. The cooled reaction mixture was then removed of water. Additional ethyl acetate (150 mL) was added and the solvent was washed three times using 100 mL portions of brine. The organic layer was dried
20 with anhydrous sodium sulfate, filtered, and the solvent concentrated. The residue purified via column chromatography using 50% ethyl acetate/hexanes as the eluents to give 2-(*o*-methoxyphenyl)quinoline.

Step 2

25

2-(*o*-Methoxyphenyl)quinoline (5.85 g, 23.1 mmol) and iridium(III) chloride trihydrate (4.07 g, 11.5 mmol) were dissolved into a solution containing 2-methoxyethanol (100 mL) and 20 mL of distilled water. The entire mixture was allowed to reflux at 100°C for 24 hours under a N₂ atmosphere. The solution was allowed to cool
30 to room temperature where the reddish solid was collected and washed with ethanol twice and dried in vacuum to give 2-(*o*-methoxyphenyl)quinoline-dichloro-bridged iridium dimer (4.53 g, 53.6% yield).

35

Step 3

2-(*o*-Methoxyphenyl)quinoline-dichloro-bridged iridium dimer (3.49 g, 2.38 mmol) and 2,4-pentanedione (0.57 g, 5.72 mmol) was added to a solution containing 2-methoxyethanol (150 mL) and sodium carbonate (2.53 g, 23.8 mmol). The mixture was allowed to stir at 105 °C for 24 hours under N₂ atmosphere. The precipitate was collected after the reaction mixture was cooled and the solids washed with water (200 mL) for 30 minutes (with stirring action). The water mixture was vacuum filtered and the solids rinsed with ethanol. The product was dried in vacuum to give bis[2-(2-methoxyphenyl)quinoline]iridium(III) acetylacetonate (1.80 g, 47.4%). The crude product was purified by sublimation.

Example 7: Synthesis of Bis[2-(3-methoxyphenyl)quinoline]iridium(III) acetylacetonate (Compound 5)

Step 1

2-Chloroquinoline (5.38 g, 32.9 mmol), and 3-methoxyphenylboronic acid (6.0 g, 39.5 mmol) were dissolved in 130 mL of ethylene glycol dimethyl ether. To the solution was added 44 mL of water of a 2M K₂CO₃ solution followed by triphenylphosphine (0.86 g, 3.29 mmol) and palladium(II) acetate (0.184 g, 0.82 mmol). The reaction mixture was stirred at reflux under N₂ atmosphere overnight. The reaction mixture was cooled and the aqueous layer discarded. An additional 200 mL of ethyl acetate was added and the solvent was washed twice with 150 mL portions of brine. The organic layer was dried with anhydrous sodium sulfate, filtered and evaporated. The crude product was purified by column chromatography on a silica gel column using 20% ethyl acetate/hexanes as the eluants. The pure fraction was collected and the solvent was reduced to give 2-(3-methoxyphenyl)quinoline (7.90 g, 94.8% yield).

Step 2

2-(3-Methoxyphenyl)quinoline (7.5 g, 29.6 mmol) and iridium(III) chloride trihydrate (5.22 g, 14.8 mmol) were stirred in 120 mL of 2-methoxyethanol and 30 mL water at reflux for 24 hours under N₂ atmosphere. The mixture was cooled to room temperature, filtered and the reddish precipitate collected was rinsed with ethanol. The

solids were then dried in vacuum to give the dichloro-bridged dimer (6.09 g, 56.2 % yield).

Step 3

5 2-(3-Methoxyphenyl)quinoline Ir dimer (4.0 g, 2.73 mmol), 2,4-pentanedione (0.68 g, 6.83 mmol) and Na₂CO₃ (2.89g 27.3 mmol) were stirred in 100 mL of 2-methoxyethanol. The reaction mixture was stirred at room temperature under N₂ atmosphere for a period of 20 hours. The precipitate was filtered and the remaining solids washed with 300 mL using water. The product was collected by vacuum filtration
10 and the solids rinsed with hexanes. The crude solid was purified on a silica gel column using 50% ethyl acetate and hexanes as the eluants to give bis[2-(3-methoxyphenyl)quinoline]iridium(III) acetylacetonate (1.35 g, 34% yield). The product was further purified by sublimation.

15 **Example 8: Synthesis of Bis[2-(4-methoxyphenyl)quinoline]iridium (III) acetylacetonate (Compound 6)**

Step 1

 2-Chloroquinoline (5.0 g, 31 mmol) and 4-methoxyphenylboronic acid (5.5 g, 36 mmol) were dissolved in a solvent mixture containing 40 mL ethylene glycol dimethyl
20 ether and 60 mL water containing 12.0 g K₂CO₃. To the stirred solution was added 1.6 g tetrakis(triphenylphosphine)palladium(0) and the mixture refluxed under N₂ overnight. The cooled reaction mixture was then removed of water, extracted with methylene chloride three times. The combined organic phase was washed with portions of brine and then dried with anhydrous sodium sulfate, filtered, and evaporated of solvent to give 2-
25 (*p*-methoxyphenyl)quinoline (5.0 g) after column chromatography (20% ethyl acetate in hexane).

Step 2

 2-(*p*-Methoxyphenyl)quinoline (4.6 g, 20 mmol) was dissolved in the solvent
30 mixture of 120 mL 2-methoxyethanol and 40 mL water and to the stirred solution was added iridium(III) chloride trihydrate (3.4 g, 10 mmol). The mixture was refluxed under N₂ atmosphere overnight. The solution was cooled down and filtered. The reddish solid

was then washed with ethanol twice and dried in vacuum to give 2-(*p*-methoxyphenyl)quinoline Ir dimer (3.6 g).

Step 3

5 2-(*p*-Methoxyphenyl)quinoline Ir dimer (3.3 g) was added to 80 mL 2-methoxyethanol and to the stirred solution was added 2,4-pentanedione (0.59 g) and sodium carbonate (2.5 g). The mixture was heated at 30 °C with stirring for 24 hours under N₂. The cooled mixture was then filtered to give bis[2-(4-methoxyphenyl)quinoline]iridium (III) acetylacetonate (1.5 g) and further purified by
10 sublimation.

Example 9: Synthesis of Bis[2-(2-trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (Compound 7)

Step 1

15 2-Chloroquinoline (7.2 g, 44.0 mmol), 2-trifluoromethylphenylboronic acid (10.0 g, 52.6 mmol), triphenylphosphine (1.16g, 4.4 mmol), palladium acetate (0.26g, 1.16 mmol) and 12 mL of a 2M solution of potassium carbonate were added together to 50 mL of ethylene glycol dimethyl ether (DME). The reaction mixture was heated under a nitrogen atmosphere and refluxed 17 hours. The mixture was cooled to room
20 temperature and the aqueous phase was separated from the organic phase. The aqueous phase was extracted with 2 X 100 mL of ethyl acetate. The combined organic extracts were washed using 1 X 150 mL of DI water, 1 X 150 mL of brine and dried over magnesium sulfate. The collected filtrate was evaporated to a crude oil. The crude product was purified by column chromatography using 80% hexanes and 20% ethyl
25 acetate as the eluants to give 2-(3-trifluorophenyl)quinoline (6.3 g).

Step 2

 2-(2-Trifluoromethylphenyl)quinoline (2.5 g, 12.1 mmol) from step 1, iridium(III) chloride (1.6 g, 4.53 mmol) were added to 60 mL of 2-ethoxyethanol and 20
30 mL of DI water and heated under nitrogen at reflux(100 °C) for 20 hours. The mixture was then cooled to room temperature and vacuum filtered. The filtered crude product was then washed with 2 X 50 mL of ethanol and 1 X 50 mL of hexane and dried in a vacuum oven to yield 2.9g (47.9%) of dimer complex.

Step 3

The dimer complex (3.4 g, 2.2 mmol) 2,4-pentanedione (5.5 g, 5.5 mmol) and sodium carbonate (2.33 g, 22 mmol) were added to 70 mL of 2-ethoxyethanol and heated
5 under nitrogen at reflux (124 °C) for 17 hours. The mixture was then cooled to room temperature and vacuum filtered. The filtered crude product was then added to 500 mL of DI water and stirred for ten minutes. The filtered crude product was then vacuum filtered and washed 2 X 150 mL of ethanol and 1 X 150 mL of hexane. The collected product was dried in a vacuum oven to give bis[2-(2-
10 trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (0.6g, 27.6%) which was further purified by vacuum sublimation.

Example 10: Synthesis of Bis[2-(3-trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (Compound 8)

Step 1

2-Chloroquinoline (1.44 g, 8.8 mmol), and 3-trifluoromethylphenylboronic acid (2.0 g, 10.5 mmol) were added to 10 mL of ethylene glycol dimethyl ether (DME) and 12 ml of a 2M solution of potassium carbonate. This was followed by the addition of triphenylphosphine (0.23 g, 0.88 mmol) and palladium acetate (0.05 g, 0.22 mmol). The
20 reaction mixture was heated at reflux (80 °C) under a nitrogen atmosphere for 17 hours. The mixture was then cooled to room temperature and the aqueous phase extracted 2 X 30 mL with ethyl acetate. The combined organic extractions were then washed with water followed by brine. The organics were dried over magnesium sulfate. The collected filtrate was then evaporated to give 2-(3-trifluorophenyl) quinoline (2.0 g,
25 83.3%) as a white solid.

Step 2

2-(3-Trimethylphenyl)quinoline (2.0g, 7.3 mmol) from step 1, and iridium(III) chloride trihydrate (1.3 g, 3.68 mmol) were added to a solution containing 40 mL of 2-
30 ethoxyethanol and 10 mL of DI water. The reaction was heated under nitrogen at reflux (100 °C) 26 hours. The mixture was then cooled to room temperature and vacuum filtered. The filtered crude product was washed with 2 X 50 mL of ethanol and 1 X 50

mL of hexanes and dried in a vacuum oven to give the dichloro-bridged dimer (1.77g, 73.8% yield).

Step 3

5 The dimer complex from step 2 above (1.77 g, 1.2 mmol), a 10-fold molar excess of 2,4-pentanedione (1.19 g, 11.9 mmol) and a 20-fold excess of sodium carbonate (2.53 g, 23.7 mmol) were added to 40 mL of 2-ethoxyethanol and heated under nitrogen at reflux (124 °C) for 18 hours. The mixture was cooled to room temperature and the precipitate was vacuum filtered. The crude product was added to 400 mL of DI water and stirred for ten minutes, vacuum filtered and washed using 2 X 50 mL of ethanol and 1 X 50 mL of hexanes. The collected product was dried in a vacuum oven to give bis[2-(3-trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (1.7g).

Example 11: Synthesis of Bis[2-(4-trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (Compound 9)

Step 1

2-Chloroquinoline (1.56g, 9.5 mmol), 4-trifluoromethylphenylboronic acid (2.17g, 11.4 mmol), triphenylphosphine (0.25g, 0.95 mmol), palladium acetate (0.05g, 0.22 mmol) and 12 mL of a 2M solution of potassium carbonate were added to 10 mL of ethylene glycol dimethyl ether (DME) and heated under nitrogen at reflux (80°C) for 18 hours. The mixture was then cooled to room temperature and the aqueous phase was separated from the organic phase. The aqueous phase was then extracted with 2 X 30 mL of ethyl acetate. The combined organic extractions were then extracted with 1 X 50 mL portion of DI water and 1 X 50 mL portion of brine and dried over magnesium sulfate. The collected filtrate was then evaporated to (2.47g, 94.7%) a crystalline solid.

Step 2

2-(4-Trimethylphenyl) quinoline (2.47g, 9.0 mmol) from step 1, iridium(III) chloride (1.59 g, 4.5 mmol) were added to 50 mL of 2-ethoxyethanol and 15 mL of water and heated under nitrogen at reflux (100 °C) for 16 hours. The mixture was cooled to room temperature and vacuum filtered. The filtered crude product was then washed with 2 X 50 mL of ethanol and 1 X 50 mL of hexane and dried in a vacuum oven to yield (1.65g, 49.2%) of the desired dimer complex.

Step 3

The dimer complex from step 2 above (1.65 g, 1.1 mmol), a 10-fold molar excess of 2,4-pentanedione (1.11 g, 11.9 mmol), and a 20-fold excess of sodium carbonate (2.36 g, 22.2 mmol) were added to 40 mL of 2-ethoxyethanol and heated under nitrogen at reflux (124 °C) for 17 hours. The mixture was cooled to room temperature and vacuum filtered. The filtered crude was added to 400 mL of water and stirred for ten minutes. The filtered crude product was vacuum filtered and washed 2 X 50 mL of ethanol and 1 X 50 mL of hexanes. The collected product was dried in a vacuum oven to give bis[2-(4-trifluoromethylphenyl)quinoline]iridium(III) acetylacetonate (1.0g). The product was purified further by vacuum sublimation.

Example 12: Synthesis of Bis[2-(2,4-difluorophenyl)quinoline]iridium(III) acetylacetonate (Compound 10)

Step 1

2-Chloroquinoline (1.20 g, 12.2 mmol), 2,4-difluorophenylboronic acid (2.32g, 14.7 mmol), were added to 10 mL of ethylene glycol dimethyl ether (DME) and 12 mL of a 2 M solution of potassium carbonate. Triphenylphosphine (0.32 g, 1.2 mmol) and palladium acetate (0.069 g, 0.3 mmol) were added to the stirred reaction mixture and refluxed for 17 hours under a nitrogen atmosphere. The mixture was cooled to room temperature and the aqueous phase was separated from the organic phase. The aqueous phase was extracted with 2 X 30 mL of ethyl acetate. The combined organic extracts were washed first with distilled water followed by brine. The solvent was dried over magnesium sulfate and concentrated to give 2-(2,4-difluorophenyl)quinoline (2.9g, 98.6%) as a white solid.

Step 2

2-(2,4-Difluorophenyl)quinoline (2.9 g, 12.1 mmol) from step 1 above and iridium(III) chloride (2.1 g, 5.96 mmol) were added to 40 mL of 2-ethoxyethanol and 10 mL of DI water and heated under nitrogen at reflux for 16 hours. The mixture was cooled to room temperature and the crude product removed by vacuum filtration. The filtered crude product was washed with 2 X 50 mL of ethanol and 1 X 50 mL of hexanes and dried in a vacuum oven to yield (2.3 g, 51.3%) of the dimer complex.

Step 3

The dimer complex from step 2 above (2.3 g, 1.6 mmol) a 10-fold molar excess of 2,4-pentanedione (1.6 g, 16 mmol) and a 20-fold excess of sodium carbonate (3.4 g, 32 mmol) were added to 40 mL of 2-ethoxyethanol and heated under nitrogen at reflux (124 °C) for 17 hours. The mixture was then cooled to room temperature and vacuum filtered. The filtered crude was then added to 400 mL of DI water and stirred for ten minutes. The filtered crude was then vacuum filtered and washed 2 X 50 mL of ethanol and 1 X 50 mL of hexane. The collected product was dried in a vacuum oven to give a bis[2-(2,4-difluorophenyl)quinoline]iridium(III) acetylacetonate (2.1 g).

Example 13: Synthesis of Bis(2-phenyl-4-methylquinoline)iridium(III) acetylacetonate (Compound 11)

Step 1

2-Chloro-4-methylquinoline (5.0 g, 30 mmol) and phenyl boronic acid (4.4 g, 36 mmol) were dissolved into 100 mL of ethylene glycol dimethyl ether. To the stirred reaction was added triphenylphosphine (0.8 g) and palladium(II) acetate, followed by 50 mL of a 2 M solution of potassium carbonate. The reaction was refluxed for 16 hours. After cooling, the aqueous layer was discarded and additional ethyl acetate added. The organics were washed with a saturated solution of sodium chloride and separated. The organic layer was dried over magnesium sulfate, concentrated, and purified on a silica gel column using 20% ethyl acetate and hexanes as the eluants. The pure fractions were combined and concentrated to give 2-phenyl-4-methylquinoline (4.0 g, 61% yield) as an oil.

Step 2

2-Phenyl-4-methylquinoline (4.0 g, 18 mmol) and iridium(III) chloride trihydrate (3.2 g, 9 mmol) were dissolved into a solution containing 80 mL of 2-methoxyethanol and 20 mL of water. The reaction mixture was refluxed for 18 hours and cooled to room temperature. The red/brown precipitate was collected by vacuum filtration and washed once with absolute ethanol followed by hexanes to give the dichloro-bridged dimer (3.0 g, 25 % yield).

Step 3

The dichloro-bridged dimer (3.0 g, 2.3 mmol) and 2,4-pentanedione (2.3 g, 23 mmol) were dissolved into a solution containing 100 mL of 2-methoxyethanol and sodium carbonate (4.8 g in 50 mL). The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 17 hours. The reaction mixture was cooled and the red precipitate was collected by vacuum filtration to give bis[2-(2,4-difluorophenyl)quinoline]iridium(III) acetylacetonate (2.1 g) as a red solid. The material was further purified by vacuum sublimation.

10 **Example 14: Synthesis of Bis(2-phenyl-3-methylquinoline)iridium(III) acetylacetonate (Compound 12)**

Step 1

2-Chloro-3-methylquinoline (5.43 g, 30.6 mmol), phenylboronic acid (4.47 g, 36.7 mmol), Pd(II) acetate (0.17g, 0.76 mmol), and triphenylphosphine (0.80 g, 3.06 mmol) were dissolved in 100 mL DME. To the stirred solution was added K₂CO₃ (11.4g dissolved into 41 mL H₂O). The entire mixture was allowed to stir at reflux for 18 hours under N₂ atmosphere. The cooled mixture was then removed of water, enriched with 150 mL of ethyl acetate, extracted three times from brine, dried over anhydrous sodium sulfate, filtered and evaporated of solvent. The crude liquid was then purified on a silica gel column using 20% ethyl acetate/hexanes. The purest fractions were combined to give 2-phenyl-3-methylquinoline (6.42 g, 95.8% yield).

Step 2

3-Methyl-2-phenylquinoline (5.80 g, 26 mmol) was stirred in 100 mL 2-methoxyethanol/25mL H₂O and to the stirred solution was added iridium (III) chloride hydrate (4.9 g, 13 mmol). The reaction mixture was allowed to stir under N₂ atmosphere at 100 °C for 24 hours. The solids were collected on a filter, and rinsed with ethanol to give the dichloro-bridged dimer (2.72 g, 30.9% yield).

30 *Step 3*

3-Methyl-2-phenylquinoline Ir dimer (2.72 g) was stirred in 80 mL 2-methoxyethanol and to the solution was added sodium carbonate (2.72 g) and 2,4-pentanedione (1.02 g). This was allowed to stir for 24 hours under N₂ atmosphere. The

reaction mixture was filtered and the solids washed with water. The solids were then filtered again and rinsed with hexanes. The amount collected gave bis(2-phenyl-3-methylquinoline)iridium(III) acetylacetonate (0.85 g, 29.8% yield). This material was purified by vacuum sublimation.

5

Example 15: Synthesis of Bis(phenylisoquinoline)iridium(III) acetylacetonate (Compound 13)

Step 1

1-Chloroisoquinoline (5.0 g, 30 mmol) and phenylboronic acid (4.5 g, 37 mmol) was dissolved into 100 mL of ethylene glycol dimethyl ether, followed by the addition of triphenylphosphine (0.7 g, 3 mmol) and Pd(II) acetate (0.17 g, 0.75 mmol). The reaction mixture was refluxed for 16 hours. The reaction mixture was cooled and the aqueous layer discarded. Additional ethyl acetate was added and the solvent was washed with a saturated solution of sodium chloride, dried over magnesium sulfate and concentrated to give 1-phenylisoquinoline (5.0 g, 79% yield)

15

Step 2

1-Phenylisoquinoline (5.0 g, 24 mmol) and iridium(III) chloride trihydrate (4.5 g, 12 mmol) was added to a solution containing 80 mL of 2-methoxyethanol and 20 mL of water. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 12 hours. The reaction mixture was cooled and the red/brown precipitate was collected by vacuum filtration and washed once with hexanes. The dichloro-bridged dimer (5.3 g, 30% yield) was dried and used directly in the next step.

20

Step 3

The dichloro-bridged dimer (2.0 g, 1.6 mmol) and 2,4-pentanedione (1.6 g, 16 mmol) were added to 100 mL of 2-methoxyethanol to which a solution of sodium carbonate (3.34 g, 50 mL) was added and the reaction mixture heated to reflux. The reaction mixture was cooled after 16 hours and the crude product collected by vacuum filtration to give bis(phenylisoquinoline)iridium(III) acetylacetonate (1.0 g). The crude material was purified by vacuum sublimation.

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As those skilled in the art will appreciate, numerous changes and modifications can be made to the preferred embodiments of the invention without departing from the

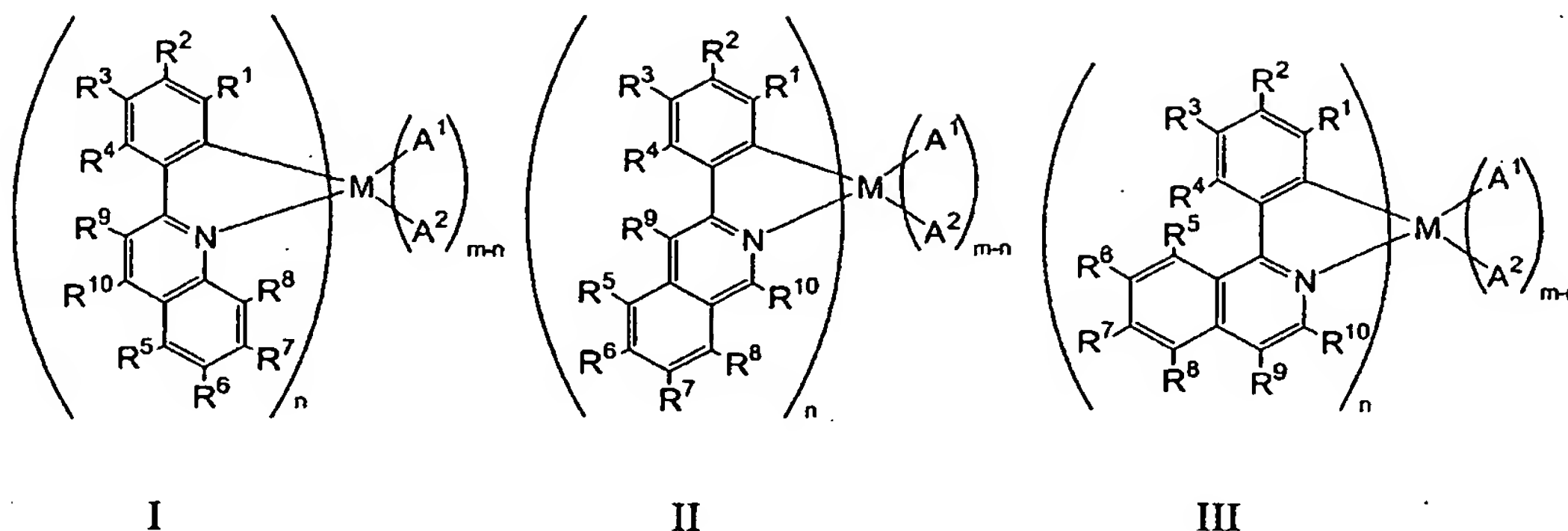
spirit of the invention. It is intended that all such variations fall within the scope of the invention. Throughout this specification, various groupings are employed to conveniently describe constituent variables of compounds and groups of various related moieties. It is specifically intended that each occurrence of such groups throughout this
5 specification include every possible subcombination of the members of the groups, including the individual members thereof.

It is intended that each of the patents, applications, and printed publications mentioned in this patent document be hereby incorporated by reference in its entirety.

10

What is claimed is:

1. A compound of Formula I, II, or III:



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, F, Cl, Br, I, R¹¹, OR¹¹, N(R¹¹)₂, P(R¹¹)₂, P(OR¹¹)₂, POR¹¹, PO₂R¹¹, PO₃R¹¹, SR¹¹, Si(R¹¹)₃, B(R¹¹)₂, B(OR¹¹)₂, C(O)R¹¹, C(O)OR¹¹, C(O)N(R¹¹)₂, CN, NO₂, SO₂, SOR¹¹, SO₂R¹¹, SO₃R¹¹; and additionally, or alternatively, any one or more of R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and R¹⁰, together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each R¹¹ is, independently, H, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ heteroalkyl, C₃-C₄₀ aryl, C₃-C₄₀ heteroaryl; wherein R¹¹ is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R¹², OR¹², N(R¹²)₂, P(R¹²)₂, P(OR¹²)₂, POR¹², PO₂R¹², PO₃R¹², SR¹², Si(R¹²)₃, B(R¹²)₂, B(OR¹²)₂, C(O)R¹², C(O)OR¹², C(O)N(R¹²)₂, CN, NO₂, SO₂, SOR¹², SO₂R¹², or SO₃R¹²;

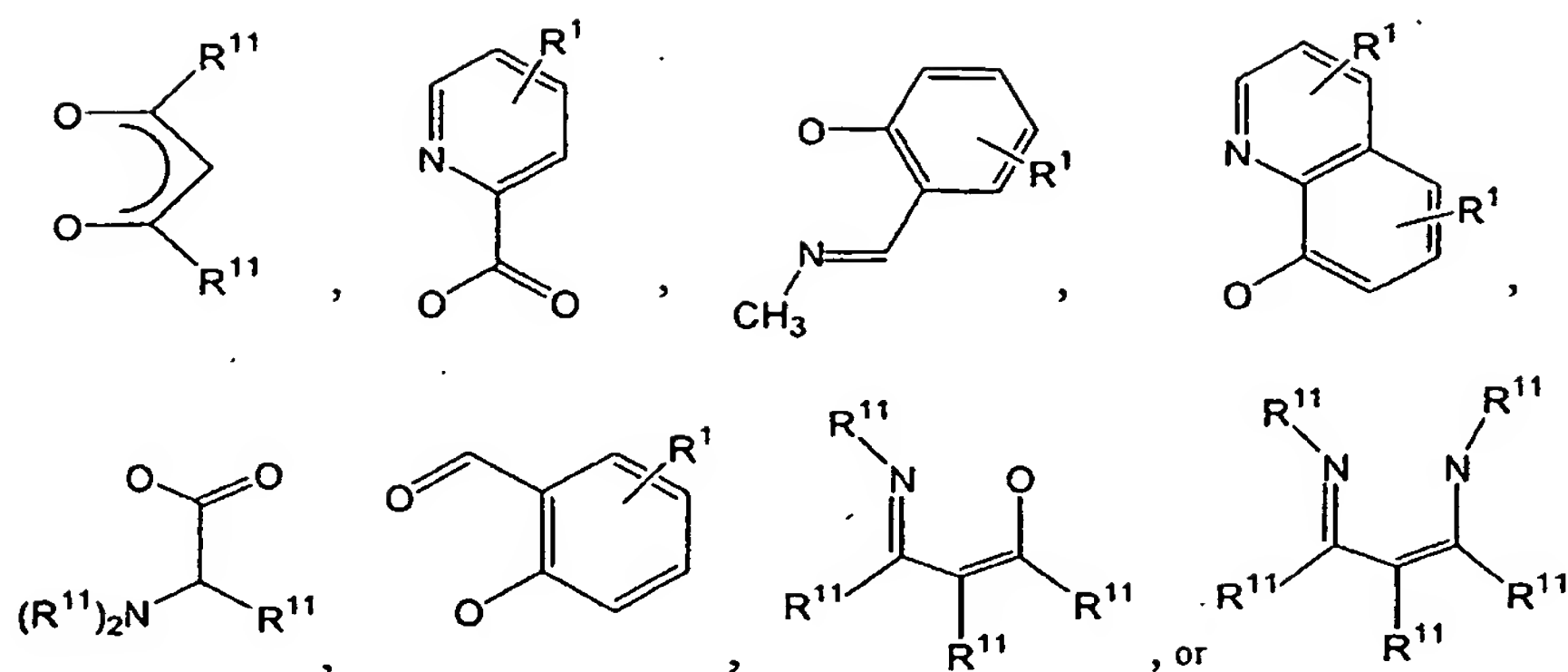
each R¹² is, independently, H, C₁-C₂₀ alkyl, C₁-C₂₀ perhaloalkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ heteroalkyl, C₃-C₄₀ aryl, or C₃-C₄₀ heteroaryl;

m is the formal charge of metal atom M;

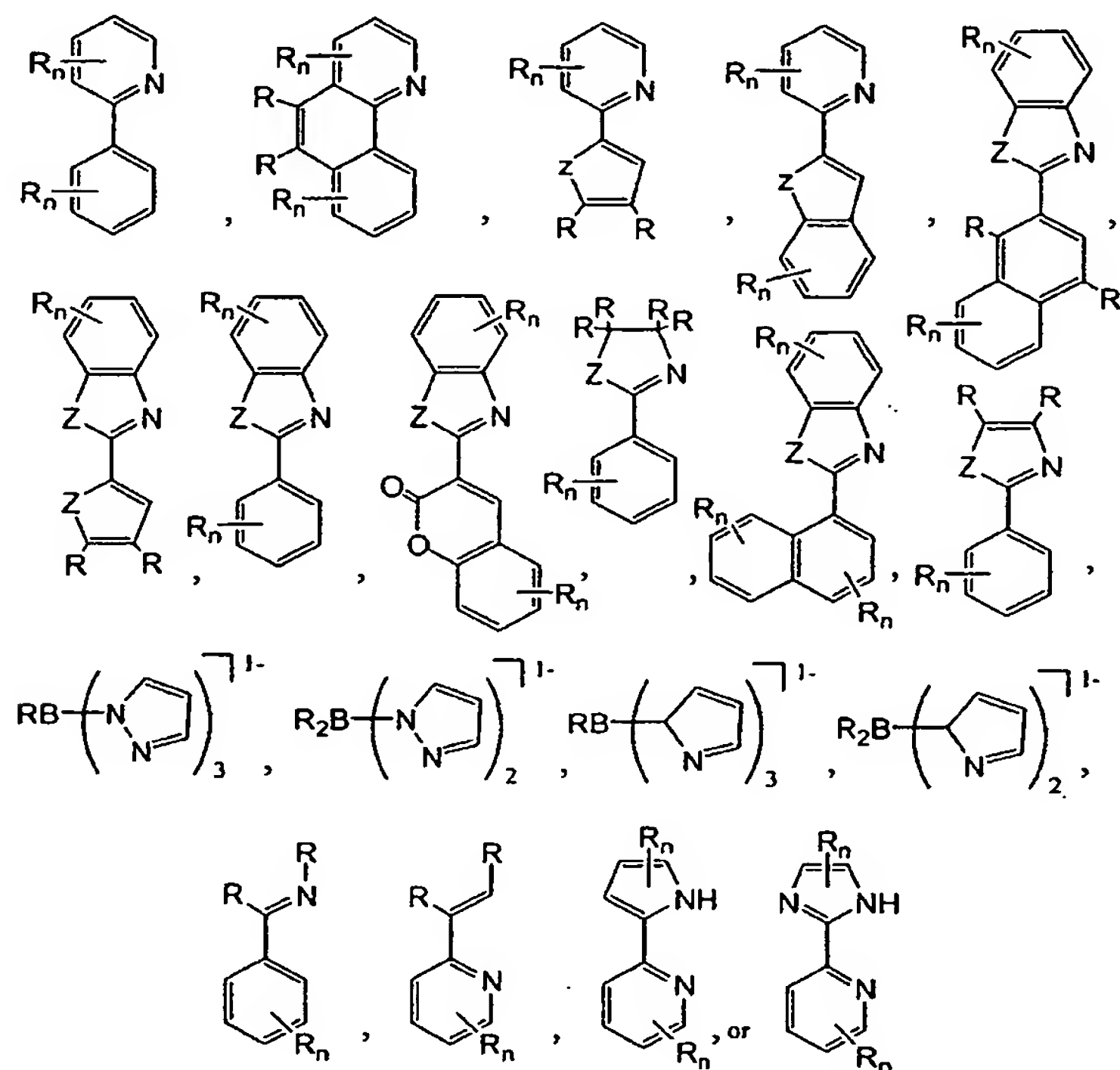
n is 1, 2 or 3; and

wherein at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is not H in compounds of Formula I.

2. A compound of claim 1 having Formula I.
3. A compound of claim 1 having Formula II.
4. A compound of claim 1 having Formula III.
5. A compound of claim 1 wherein M is a heavy metal.
6. A compound of claim 1 wherein M is Ir, Os, Pt, Pb, Re, or Ru.
7. A compound of claim 1 wherein M is Ir.
8. A compound of claim 1 wherein M is Pt.
9. A compound of claim 1 wherein A^1 and A^2 are monodentate ligands.
10. A compound of claim 1 wherein A^1 and A^2 are monodentate ligands having a combined charge of (-1).
11. A compound of claim 1 wherein A^1 or A^2 is F, Cl, Br, I, CO, CN, $CN(R^{11})$, SR^{11} , SCN, OCN, $P(R^{11})_3$, $P(OR^{11})_3$, $N(R^{11})_3$, NO, N_3 , or a nitrogen-containing heterocycle optionally substituted by one or more substituents X.
12. A compound of claim 1 wherein A^1 and A^2 are covalently joined together to form a bidentate ligand.
13. A compound of claim 1 wherein said bidentate ligand is monoanionic.
14. A compound of claim 1 wherein said bidentate ligand is



15. A compound of claim 1 wherein said bidentate ligand coordinates through a carbon atom and a nitrogen atom.
16. A compound of claim 15 wherein said bidentate ligand is a biaryl compound.
17. A compound of claim 1 wherein said bidentate ligand is

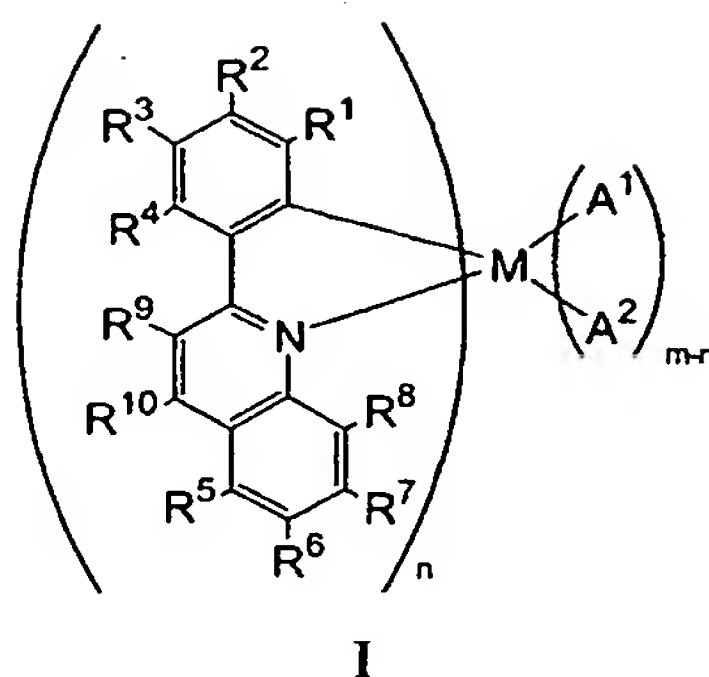


wherein:

Z is O, S, or NR;

each R is, independently, R¹¹; and
n is 0 to 5.

18. A compound of claim 1 wherein said bidentate ligand is acetylacetonate.
19. A compound of claim 1 wherein each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, CH₃, CF₃, OCH₃, or F.
20. A compound of claim 1 wherein at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is methyl.
21. A compound of claim 1 wherein at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is trifluoromethyl.
22. A compound of claim 1 wherein at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is methoxy.
23. A compound of claim 1 wherein at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is fluoro.
24. A compound of claim 1 wherein at least one of said R³, R⁴, R⁹, and R¹⁰ is other than H.
25. A compound of claim 1 having a photoluminescence maximum at a wavelength of from about 550 to about 700 nm.
26. A composition comprising a compound of claim 1.
27. The composition of claim 26 further comprising BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃, BAlq, Flrpic, or Irppy.
28. A compound of Formula I



wherein:

M is a metal atom;

each A^1 and A^2 is, independently, a monodentate ligand; or A^1 and A^2 are covalently joined together to form a bidentate ligand;

each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is, independently, H, an activating group, or a deactivating group; and additionally, or alternatively, any one or more of R^1 and R^2 , or R^2 and R^3 , or R^3 and R^4 , or R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 , or R^9 and R^{10} , together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R^{12} , OR^{12} , $N(R^{12})_2$, $P(R^{12})_2$, $P(OR^{12})_2$, POR^{12} , PO_2R^{12} , PO_3R^{12} , SR^{12} , $Si(R^{12})_3$, $B(R^{12})_2$, $B(OR^{12})_2$, $C(O)R^{12}$, $C(O)OR^{12}$, $C(O)N(R^{12})_2$, CN, NO_2 , SO_2 , SOR^{12} , SO_2R^{12} , or SO_3R^{12} ;

each R^{12} is, independently, H, C_1 - C_{20} alkyl, C_1 - C_{20} perhaloalkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, or C_3 - C_{40} heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

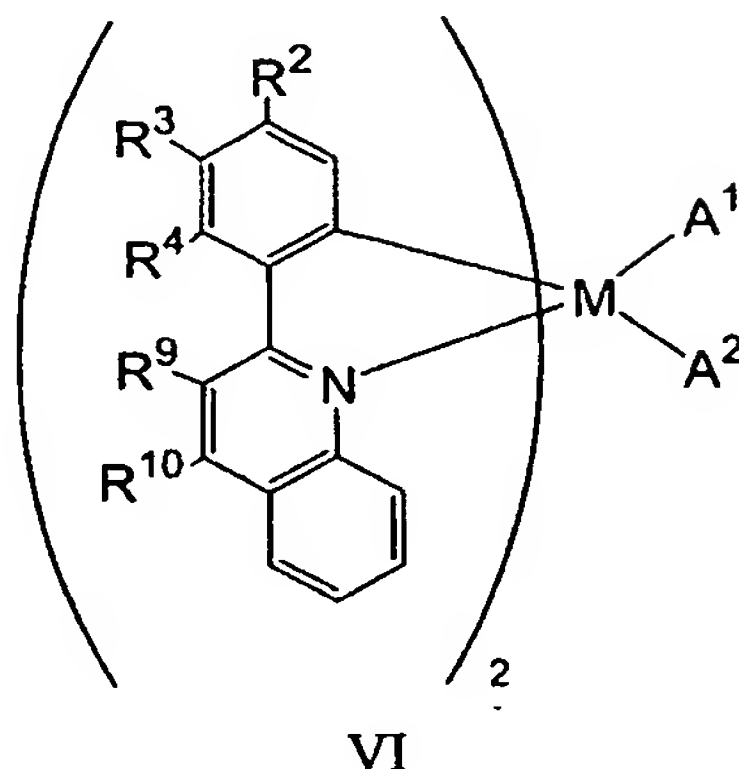
wherein at least one of R^3 , R^9 , and R^{10} is an activating group, or wherein at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group.

29. The compound of claim 28 wherein at least one of R^3 , R^9 , and R^{10} is an activating group.

30. The compound of claim 29 wherein said activating group is alkyl, heteroalkyl, aryl, heteroaryl, alkoxy, aryloxy, hydroxy, mercapto, thiolato, amino, phosphino, alkylcarbonylamino, or arylcarbonylamino.
31. The compound of claim 29 wherein said activating group is methyl or methoxy.
32. The compound of claim 28 wherein at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group.
33. The compound of claim 32 wherein said deactivating group is halo, cyano, nitro, aldehyde, alkylcarbonyl, arylcarbonyl, ammonium, perhaloalkyl, carboxylic acid, alkoxycarbonyl, aryloxycarbonyl, or sulfo.
34. The compound of claim 32 wherein said deactivating group is F or CF_3 .
35. The compound of claim 28 wherein at least two of said R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} are activating or deactivating groups.
36. The compound of claim 28 wherein A^1 and A^2 are covalently joined together to form a bidentate ligand.
37. The compound of claim 28 wherein said bidentate ligand is monoanionic.
38. The compound of claim 28 wherein said bidentate ligand is acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate.
39. The compound of claim 28 wherein said bidentate ligand is acetylacetonate.
40. A compound of claim 28 wherein M is a heavy metal.
41. A compound of claim 28 wherein M is Ir, Os, Pt, Pb, Re, or Ru.
42. A compound of claim 28 wherein M is Ir.

43. A compound of claim 28 wherein M is Pt.

44. A compound of Formula VI



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand; and

R⁴ is F; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is OCH₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R³ is OCH₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² is OCH₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is CF₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R³ is CF₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² is CF₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² and R⁴ are each F; and R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each, independently, H, an activating group or deactivating group.

45. The compound of claim 44 wherein A^1 and A^2 are covalently joined together to form a bidentate ligand.

46. The compound of claim 44 wherein said bidentate ligand is monoanionic.

47. The compound of claim 44 wherein said bidentate ligand is acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate.

48. The compound of claim 44 wherein said bidentate ligand is acetylacetonate.

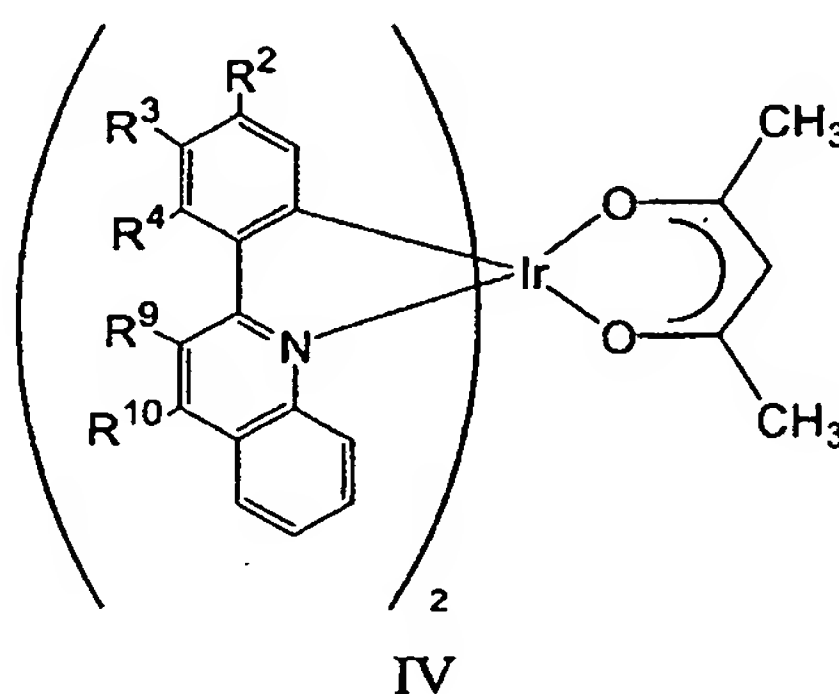
49. A compound of claim 44 wherein M is a heavy metal.

50. A compound of claim 44 wherein M is Ir, Os, Pt, Pb, Re, or Ru.

51. A compound of claim 44 wherein M is Ir.

52. A compound of claim 44 wherein M is Pt.

53. A compound of Formula IV



wherein:

R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H; or
 R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H; or
 R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H; or
 R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

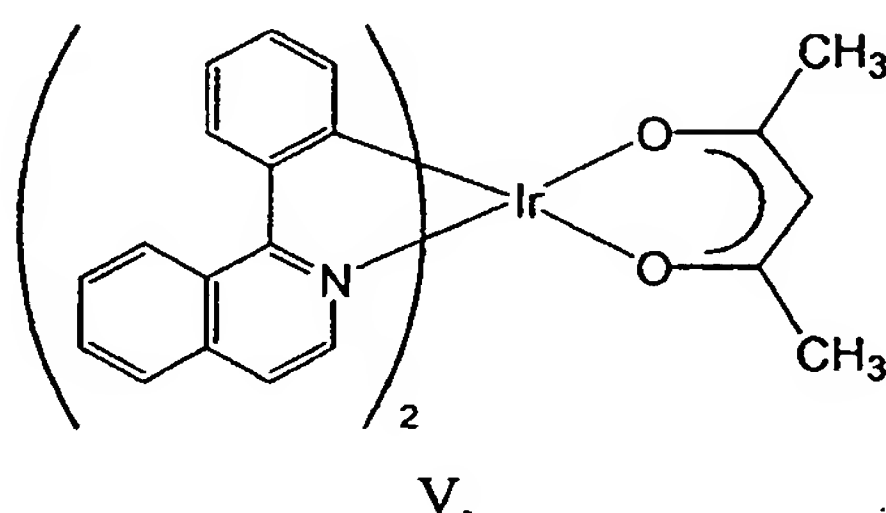
54. The compound of claim 53 wherein R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H.
55. The compound of claim 53 wherein R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H.
56. The compound of claim 53 wherein R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H.
57. The compound of claim 53 wherein R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H.
58. The compound of claim 53 wherein R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H.
59. The compound of claim 53 wherein R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H.
60. The compound of claim 53 wherein R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H.
61. The compound of claim 53 wherein R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H.

62. The compound of claim 53 wherein R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H.

63. The compound of claim 53 wherein R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H.

64. The compound of claim 53 wherein R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

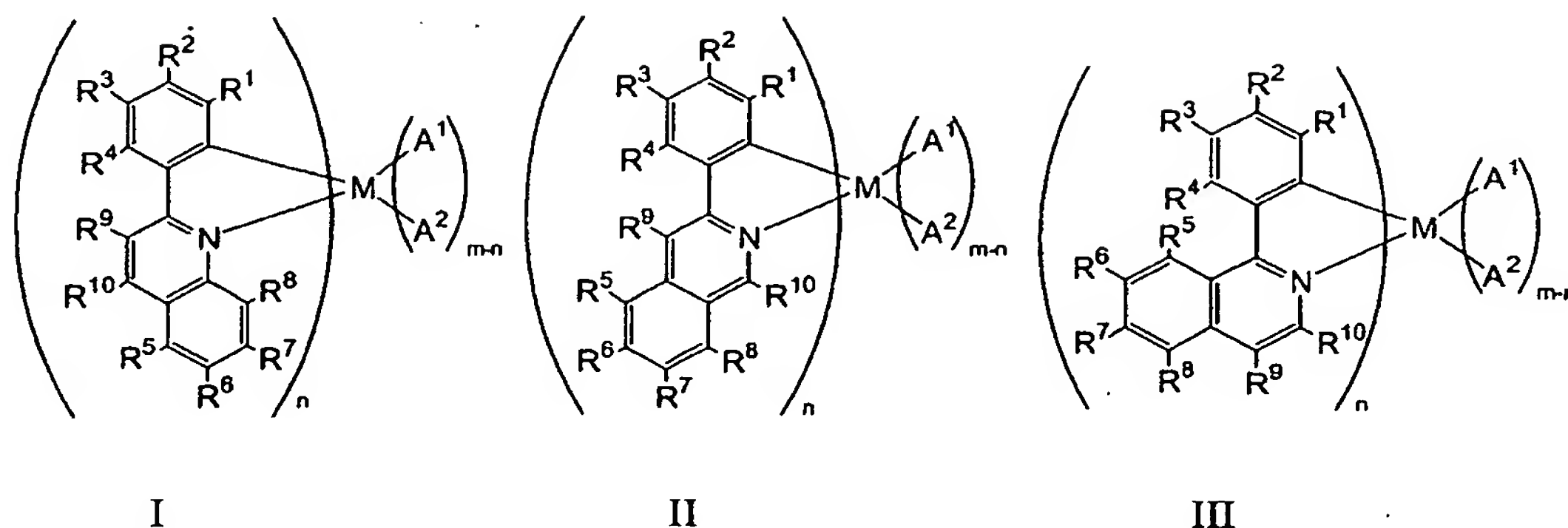
65. A compound of Formula V



66. A method of increasing the wavelength of a photoluminescence maximum for a compound of claim 1, said method comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is an activating group that influences the HOMO energy level of said compound, or at least one of said substituents is a deactivating group that influences the LUMO energy level of said compound.

67. A method of decreasing the wavelength of a photoluminescence maximum for a compound of claim 1, said method comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is a deactivating group that influences the HOMO energy level of said compound, or at least one of said substituents is an activating group that influences the LUMO energy level of said compound.

68. An organic light emitting device comprising a compound of Formula I, II, or III



wherein:

M is a metal atom;

each A^1 and A^2 is, independently, a monodentate ligand; or A^1 and A^2 are covalently joined together to form a bidentate ligand;

each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is, independently, H, F, Cl, Br, I, R^{11} , OR^{11} , $N(R^{11})_2$, $P(R^{11})_2$, $P(OR^{11})_2$, POR^{11} , PO_2R^{11} , PO_3R^{11} , SR^{11} , $Si(R^{11})_3$, $B(R^{11})_2$, $B(OR^{11})_2$, $C(O)R^{11}$, $C(O)OR^{11}$, $C(O)N(R^{11})_2$, CN, NO_2 , SO_2 , SOR^{11} , SO_2R^{11} , SO_3R^{11} ; and additionally, or alternatively, any one or more of R^1 and R^2 , or R^2 and R^3 , or R^3 and R^4 , or R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 , or R^9 and R^{10} , together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each R^{11} is, independently, H, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, C_3 - C_{40} heteroaryl; wherein R^{11} is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R^{12} , OR^{12} , $N(R^{12})_2$, $P(R^{12})_2$, $P(OR^{12})_2$, POR^{12} , PO_2R^{12} , PO_3R^{12} , SR^{12} , $Si(R^{12})_3$, $B(R^{12})_2$, $B(OR^{12})_2$, $C(O)R^{12}$, $C(O)OR^{12}$, $C(O)N(R^{12})_2$, CN, NO_2 , SO_2 , SOR^{12} , SO_2R^{12} , or SO_3R^{12} ;

each R^{12} is, independently, H, C_1 - C_{20} alkyl, C_1 - C_{20} perhaloalkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} heteroalkyl, C_3 - C_{40} aryl, or C_3 - C_{40} heteroaryl;

m is the formal charge of metal atom M;

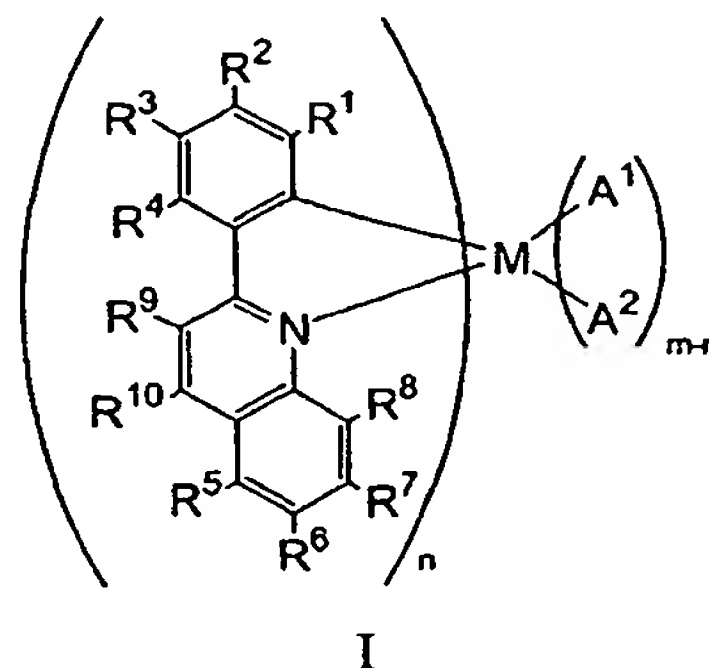
n is 1, 2 or 3; and

wherein at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is not H in compounds of Formula I.

69. The device of claim 68 wherein said compound has Formula I.
70. The device of claim 68 wherein said compound has Formula II.
71. The device of claim 68 wherein said compound has Formula III.
72. The device of claim 68 wherein said device includes an emissive layer comprising said compound.
73. The device of claim 72 wherein said emissive layer consists essentially of said compound.
74. The device of claim 72 wherein said emissive layer comprises host material doped with said compound.
75. The device of claim 74 wherein said compound comprises from about 1 to about 20 wt% of said emissive layer.
76. The device of claim 74 wherein said host material comprises BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃, or BAlq.
77. The device of claim 74 wherein said emissive layer further comprises FIrpic or Irppy.
78. The device of claim 68 having an electroluminescence maximum of from about 550 to about 700 nm.
79. The device of claim 68 having color index coordinates (CIE) of from about 0.5 to about 0.8 for x and about 0.2 to about 0.5 for y .
80. The device of claim 68 having an external quantum efficiency greater than about 4% at a brightness greater than about 10 cd/m².

81. The device of claim 68 having an external quantum efficiency greater than about 4% at a brightness greater than about 100 cd/m².

82. An organic light emitting device comprising a compound of Formula I



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is, independently, H, an activating group, or a deactivating group; and additionally, or alternatively, any one or more of R¹ and R², or R² and R³, or R³ and R⁴, or R⁵ and R⁶, or R⁶ and R⁷, or R⁷ and R⁸, or R⁹ and R¹⁰, together form, independently, a fused 4- to 7-member cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein said cyclic group is optionally substituted by one or more substituents X;

each X is, independently, H, F, Cl, Br, I, R¹², OR¹², N(R¹²)₂, P(R¹²)₂, P(OR¹²)₂, POR¹², PO₂R¹², PO₃R¹², SR¹², Si(R¹²)₃, B(R¹²)₂, B(OR¹²)₂, C(O)R¹², C(O)OR¹², C(O)N(R¹²)₂, CN, NO₂, SO₂, SOR¹², SO₂R¹², or SO₃R¹²;

each R¹² is, independently, H, C₁-C₂₀ alkyl, C₁-C₂₀ perhaloalkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ heteroalkyl, C₃-C₄₀ aryl, or C₃-C₄₀ heteroaryl;

m is the formal charge of metal atom M;

n is 1, 2 or 3; and

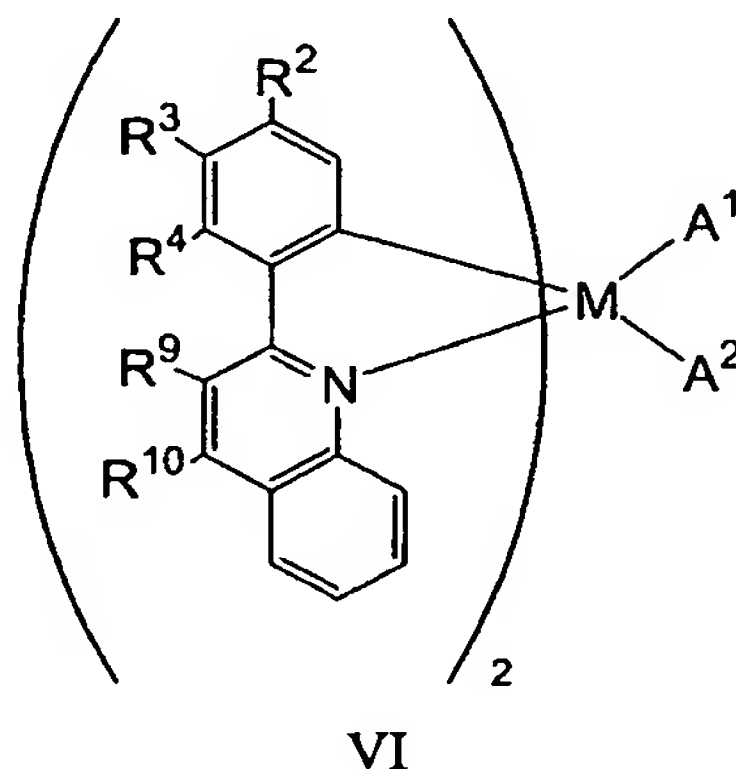
wherein at least one of R³, R⁹, and R¹⁰ is an activating group, or wherein at least one of R³, R⁴, R⁹, and R¹⁰ is a deactivating group.

83. The device of claim 82 wherein at least one of R^3 , R^9 , and R^{10} is an activating group.
84. The device of claim 83 wherein said activating group is alkyl, heteroalkyl, aryl, heteroaryl, alkoxy, aryloxy, hydroxy, mercapto, thiolato, amino, phosphino, alkylcarbonylamino, or arylcarbonylamino.
85. The device of claim 83 wherein said activating group is methyl or methoxy.
86. The device of claim 82 wherein at least one of R^3 , R^4 , R^9 , and R^{10} is a deactivating group.
87. The device of claim 86 wherein said deactivating group is halo, cyano, nitro, aldehyde, alkylcarbonyl, arylcarbonyl, ammonium, perhaloalkyl, carboxylic acid, alkoxycarbonyl, aryloxycarbonyl, or sulfo.
88. The device of claim 86 wherein said deactivating group is F or CF_3 .
89. The device of claim 82 wherein at least two of said R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} are activating or deactivating groups.
90. The device of claim 82 wherein A^1 and A^2 are covalently joined together to form a bidentate ligand.
91. The device of claim 82 wherein said bidentate ligand is monoanionic.
92. The device of claim 82 wherein said bidentate ligand is acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate.
93. The device of claim 82 wherein said bidentate ligand is acetylacetonate.
94. A device of claim 82 wherein M is a heavy metal.

95. A device of claim 82 wherein M is Ir, Os, Pt, Pb, Re, or Ru.
96. A device of claim 82 wherein M is Ir.
97. A device of claim 82 wherein M is Pt.
98. The device of claim 82 wherein said device includes an emissive layer comprising said compound.
99. The device of claim 98 wherein said emissive layer consists essentially of said compound.
100. The device of claim 98 wherein said emissive layer comprises host material doped with said compound.
101. The device of claim 100 wherein said compound comprises from about 1 to about 20 wt% of said emissive layer.
102. The device of claim 100 wherein said host material comprises BCP, CBP, OXD7, TAZ, CuPc, NPD, Alq₃, or BAlq.
103. The device of claim 100 wherein said emissive layer further comprises FIrpic or Irppy.
104. The device of claim 82 having an electroluminescence maximum of from about 550 to about 700 nm.
105. The device of claim 82 having color index coordinates (CIE) of from about 0.5 to about 0.8 for x and about 0.2 to about 0.5 for y.
106. The device of claim 82 having an external quantum efficiency greater than about 4% at a brightness greater than about 10 cd/m².

107. The device of claim 82 having an external quantum efficiency greater than about 4% at a brightness greater than about 100 cd/m².

108. An organic light emitting device comprising a compound of Formula VI



wherein:

M is a metal atom;

each A¹ and A² is, independently, a monodentate ligand; or A¹ and A² are covalently joined together to form a bidentate ligand; and

R⁴ is F; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is OCH₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R³ is OCH₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² is OCH₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R⁴ is CF₃; and R², R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R³ is CF₃; and R², R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² is CF₃; and R³, R⁴, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R² and R⁴ are each F; and R³, R⁹, and R¹⁰ are each, independently, H, an activating group or deactivating group; or

R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each, independently, H, an activating group or deactivating group; or

R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each, independently, H, an activating group or deactivating group.

109. The device of claim 108 wherein A^1 and A^2 are covalently joined together to form a bidentate ligand.

110. The device of claim 108 wherein said bidentate ligand is monoanionic.

111. The device of claim 108 wherein said bidentate ligand is acetylacetonate (acac), picolinate (pic), hexafluoroacetylacetonate, salicylidene, or 8-hydroxyquinolate.

112. The device of claim 108 wherein said bidentate ligand is acetylacetonate.

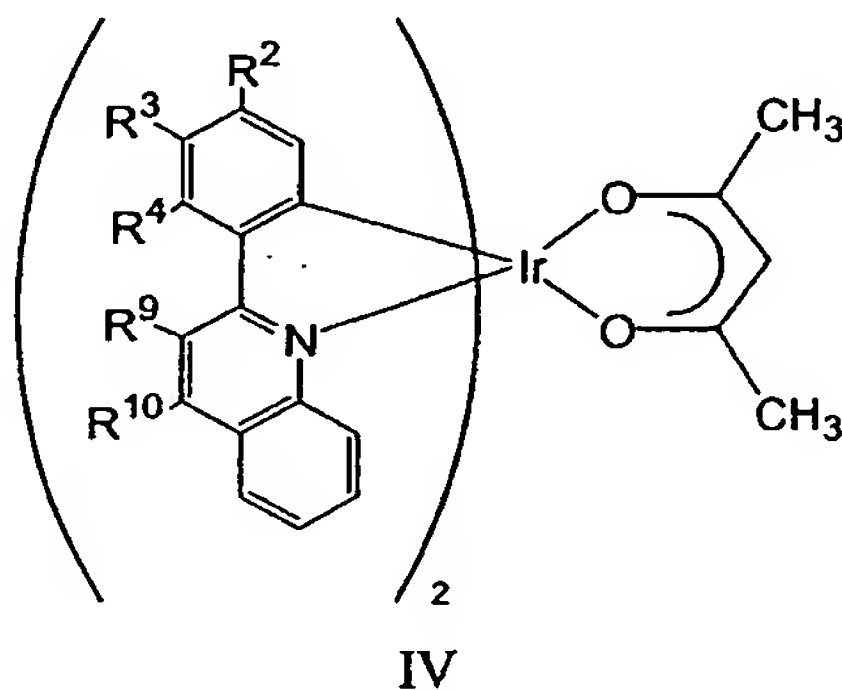
113. A device of claim 108 wherein M is a heavy metal.

114. A device of claim 108 wherein M is Ir, Os, Pt, Pb, Re, or Ru.

115. A device of claim 108 wherein M is Ir.

116. A device of claim 108 wherein M is Pt.

117. An organic light emitting device comprising a compound of Formula IV



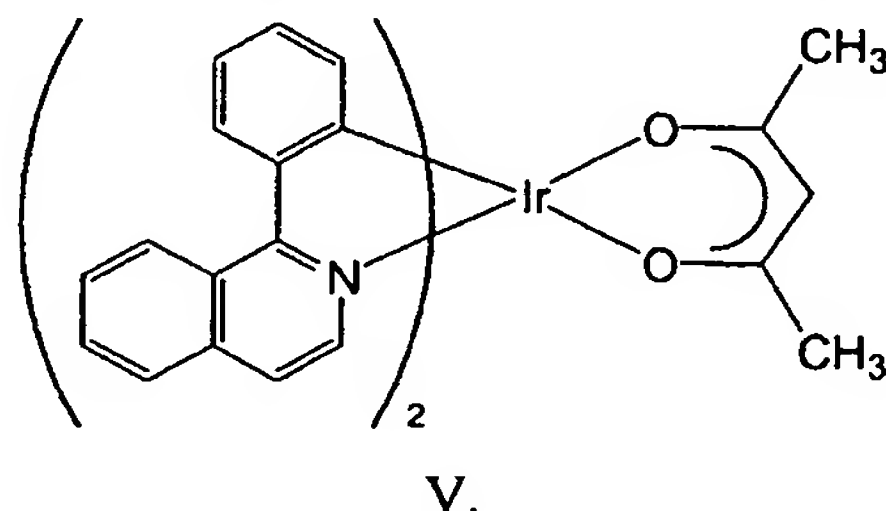
wherein:

R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H; or
 R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H; or
 R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H; or
 R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H; or
 R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H; or
 R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H; or
 R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

118. The device of claim 117 wherein R^4 is F; and R^2 , R^3 , R^9 , and R^{10} are each H.
119. The device of claim 117 wherein R^4 is OCH_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H.
120. The device of claim 117 wherein R^3 is OCH_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H.
121. The device of claim 117 wherein R^2 is OCH_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H.
122. The device of claim 117 wherein R^4 is CF_3 ; and R^2 , R^3 , R^9 , and R^{10} are each H.
123. The device of claim 117 wherein R^3 is CF_3 ; and R^2 , R^4 , R^9 , and R^{10} are each H.
124. The device of claim 117 wherein R^2 is CF_3 ; and R^3 , R^4 , R^9 , and R^{10} are each H.
125. The device of claim 117 wherein R^2 and R^4 are each F; and R^3 , R^9 , and R^{10} are each H.
126. The device of claim 117 wherein R^4 and R^{10} are each CH_3 ; and R^2 , R^3 , and R^9 are each H.
127. The device of claim 117 wherein R^9 is CH_3 ; and R^2 , R^3 , R^4 , and R^{10} are each H.

128. The device of claim 119 wherein R^{10} is CH_3 ; and R^2 , R^3 , R^4 , and R^9 are each H.

129. An organic light emitting device comprising a compound of Formula V



130. A method of increasing the wavelength of an electroluminescence maximum of an organic light emitting device comprising a compound of claim 1, said method comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is an activating group that influences the HOMO energy level of said compound, or at least one of said substituents is a deactivating group that influences the LUMO energy level of said compound.

131. A method of decreasing the wavelength of an electroluminescence maximum of an organic light emitting device comprising a compound of claim 1, said method comprising choosing substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} such that at least one of said substituents is a deactivating group that influences the HOMO energy level of said compound, or at least one of said substituents is an activating group that influences the LUMO energy level of said compound.

132. A pixel comprising the device of claim 68.

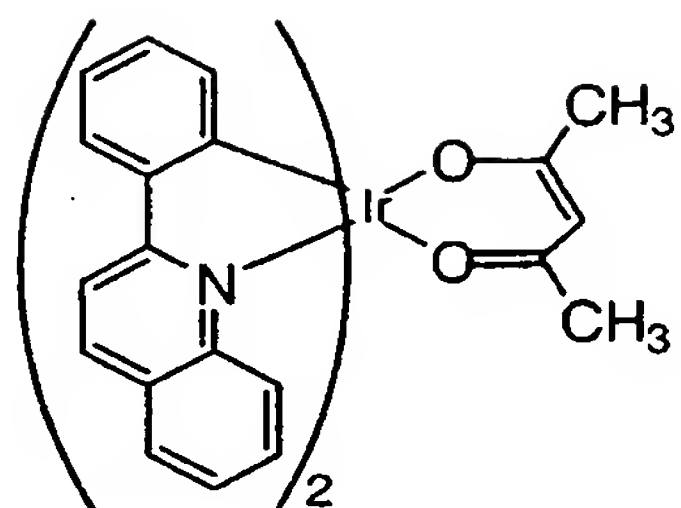
133. A pixel comprising the device of claim 82.

134. A pixel comprising the device of claim 108.

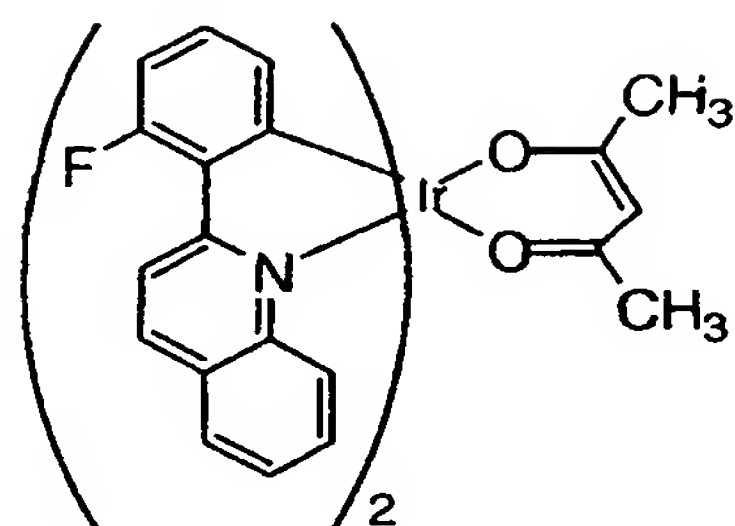
135. A pixel comprising the device of claim 117.

- 136. A pixel comprising the device of claim 129.
- 137. An electronic display comprising the device of claim 68.
- 138. An electronic display comprising the device of claim 82.
- 139. An electronic display comprising the device of claim 108.
- 140. An electronic display comprising the device of claim 117.
- 141. An electronic display comprising the device of claim 129.

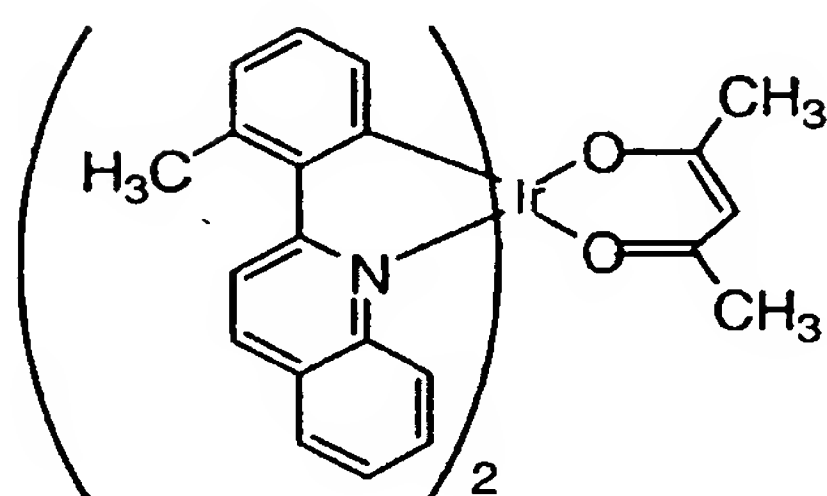
FIGURE 1



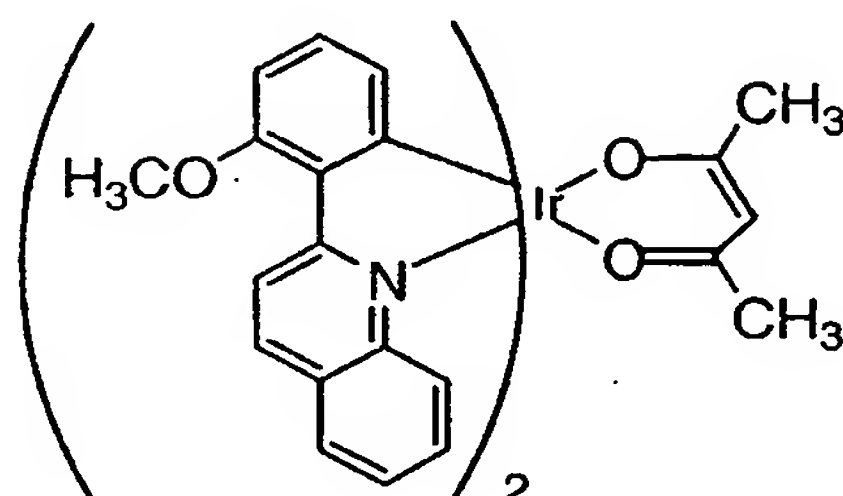
Compound 1



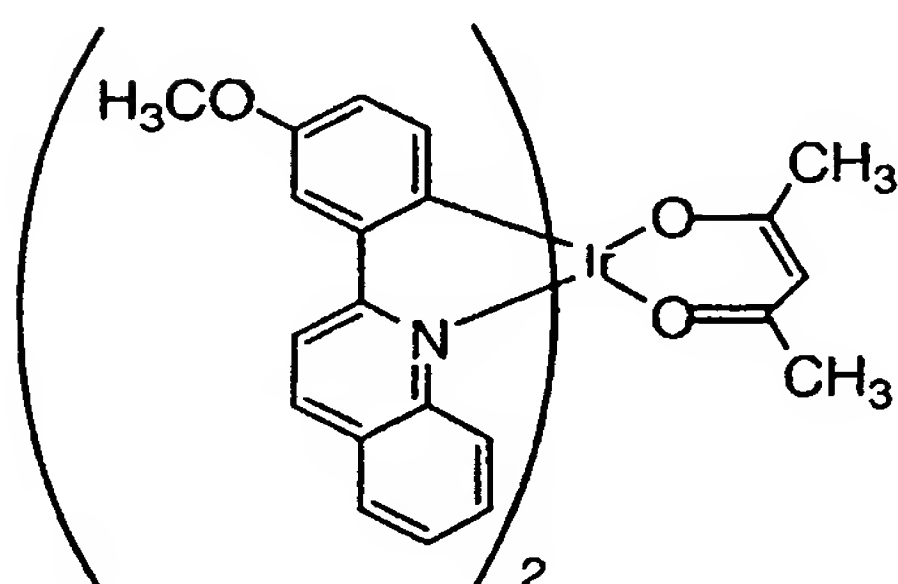
Compound 2



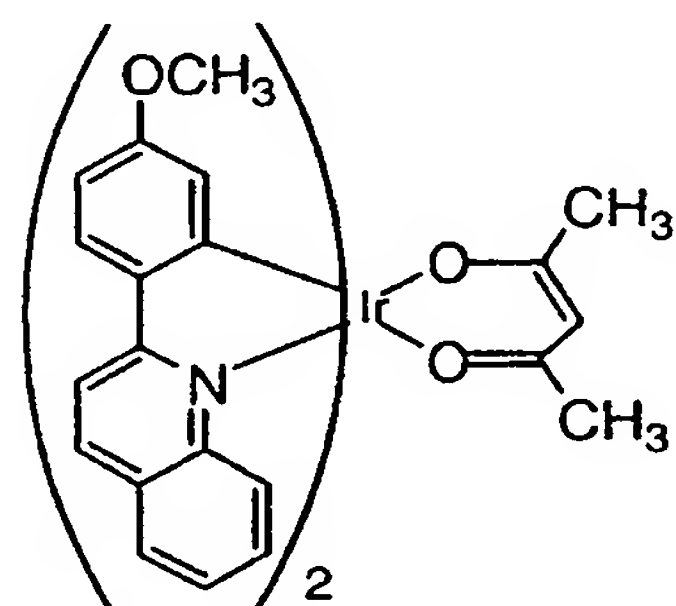
Compound 3



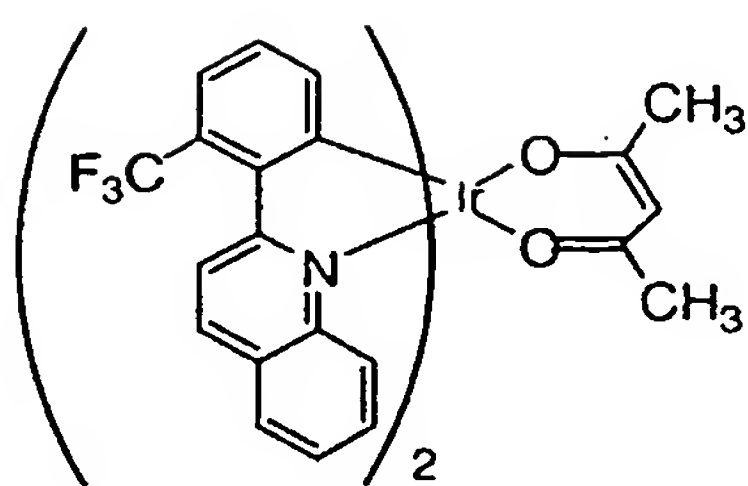
Compound 4



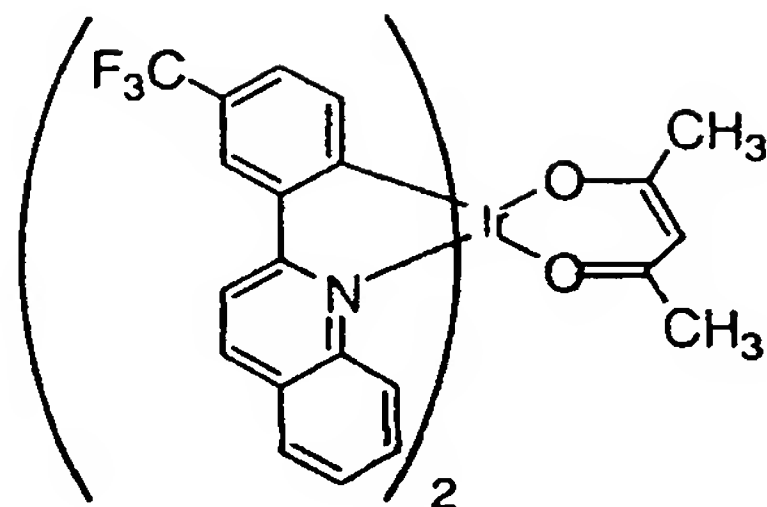
Compound 5



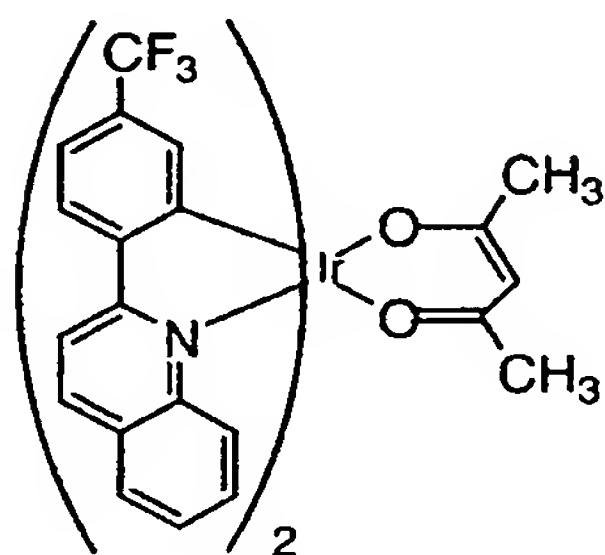
Compound 6

FIGURE 2

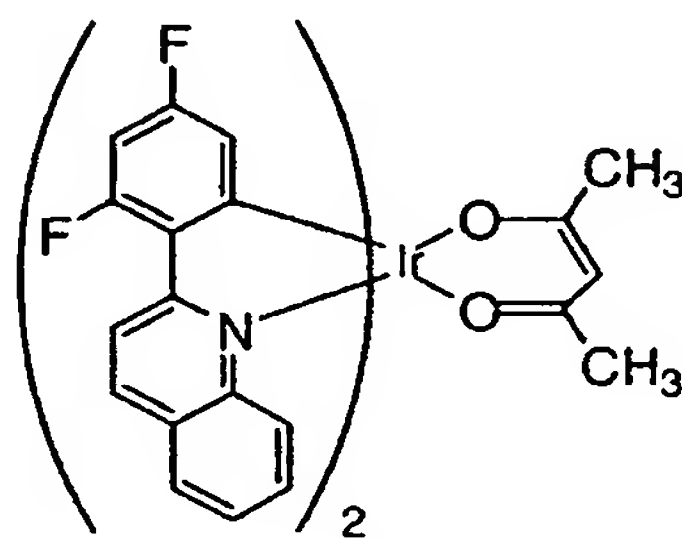
Compound 7



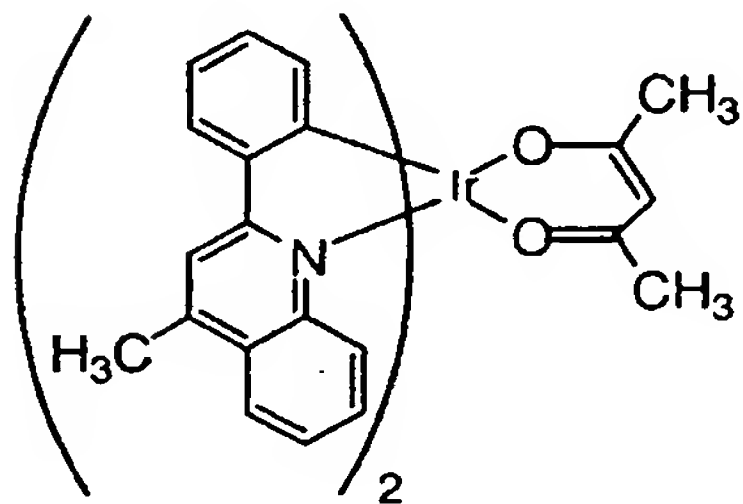
Compound 8



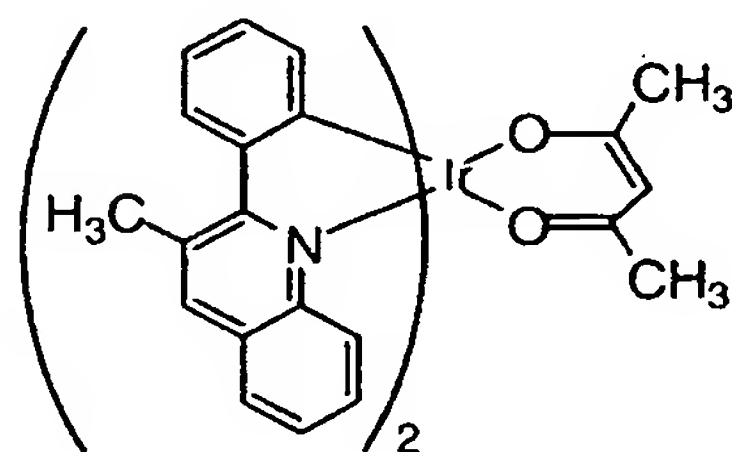
Compound 9



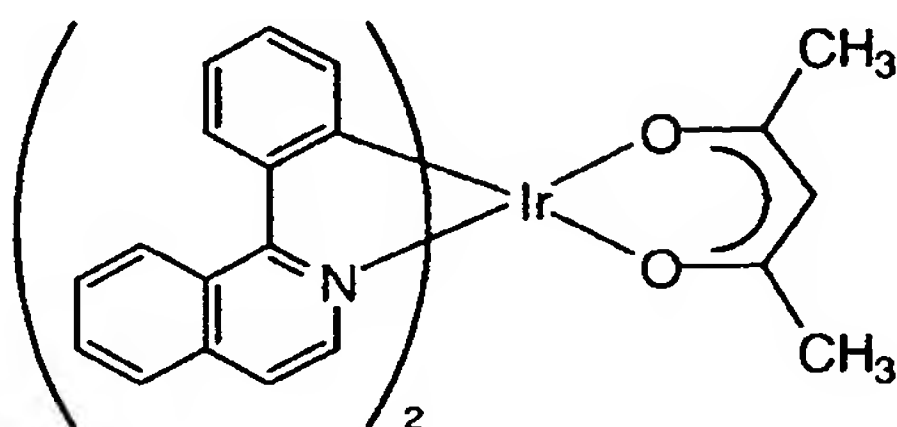
Compound 10



Compound 11



Compound 12



Compound 13

FIGURE 3

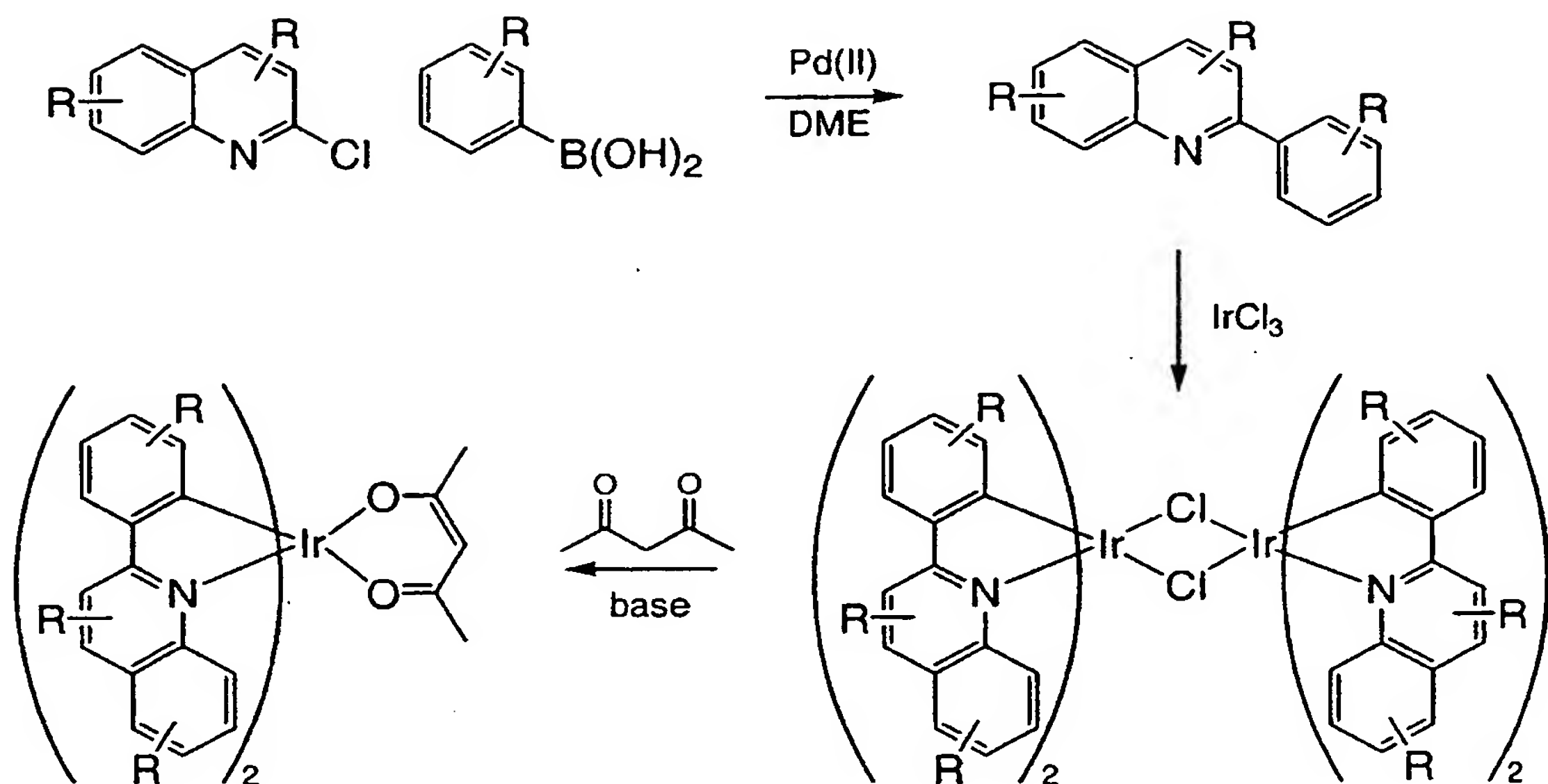


FIGURE 4

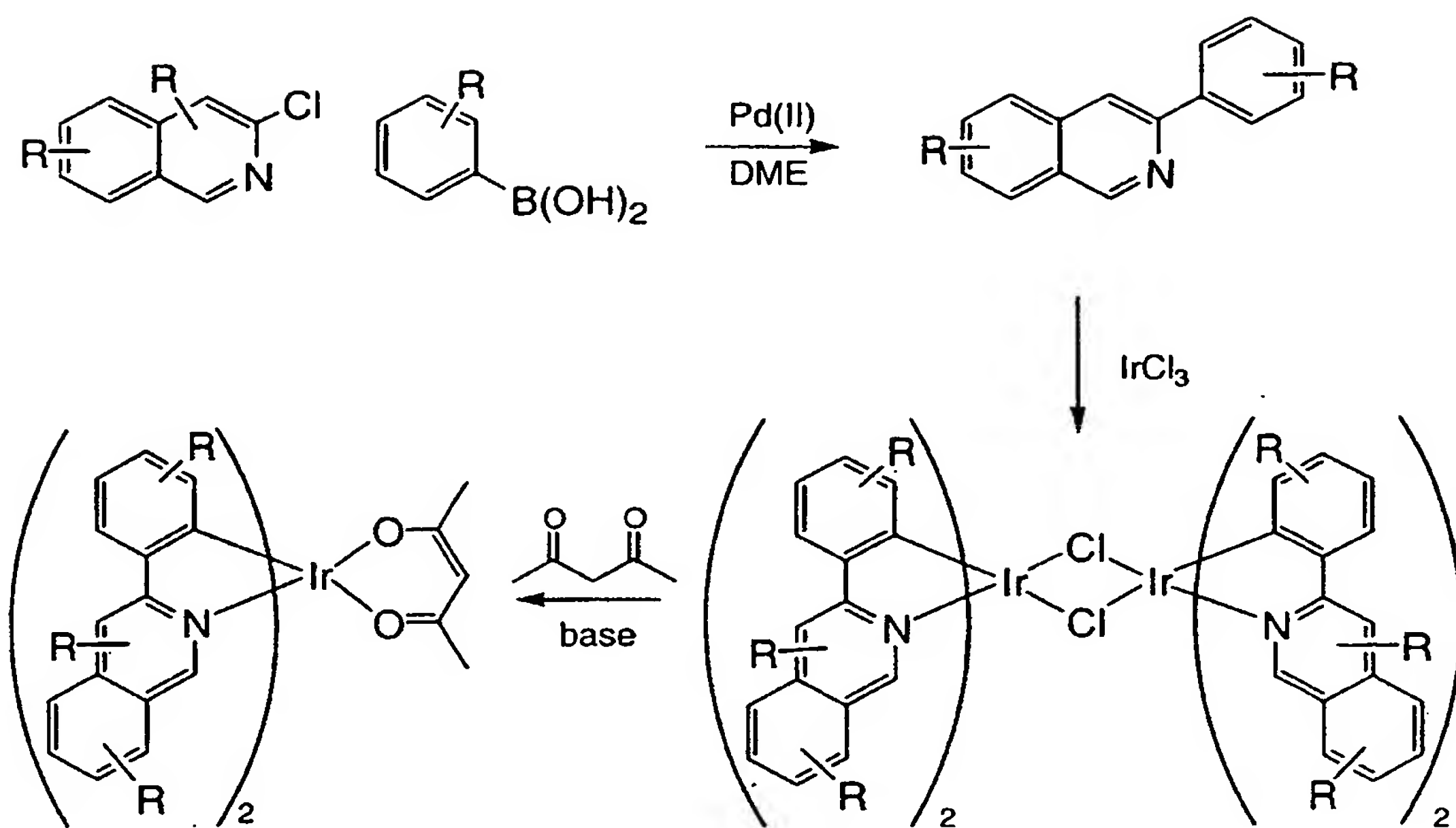


FIGURE 5

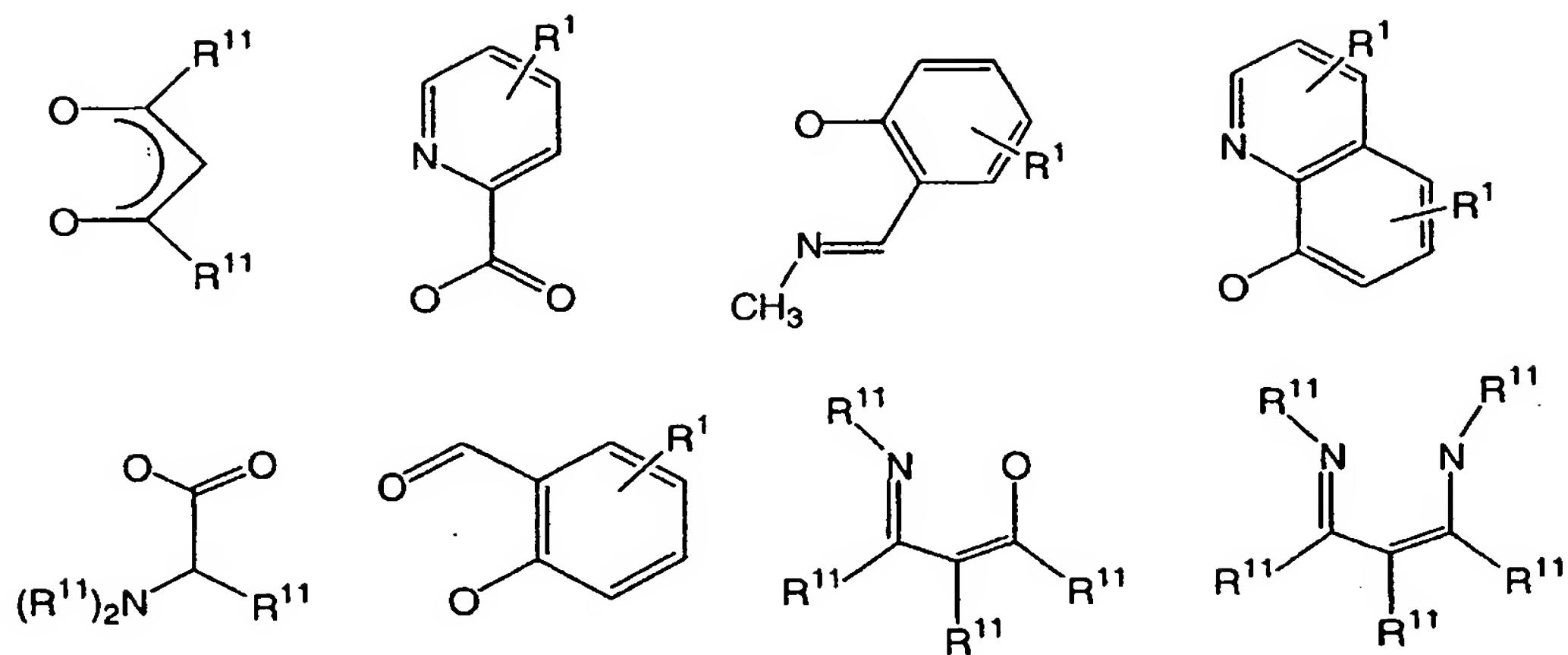


FIGURE 6

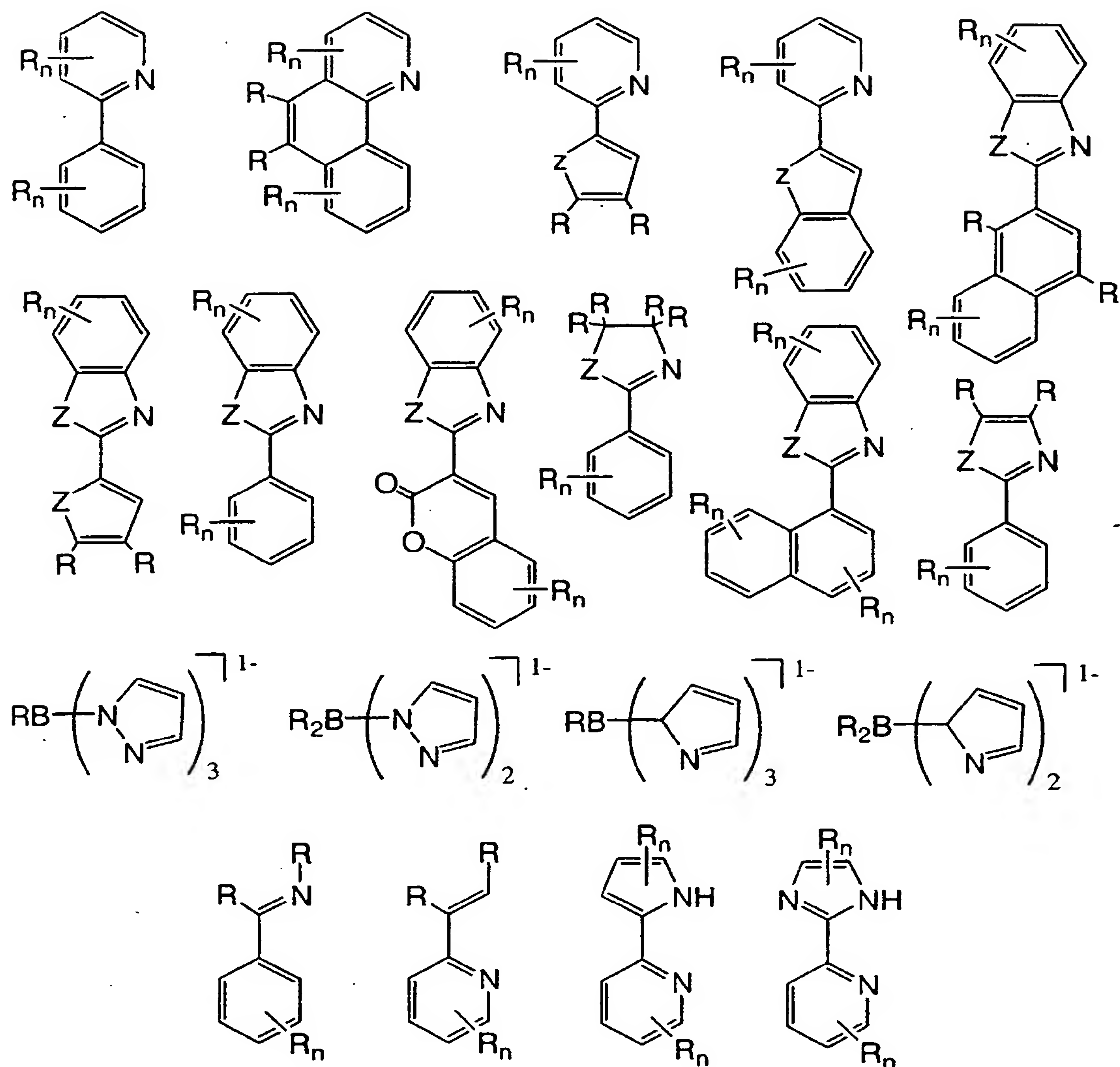
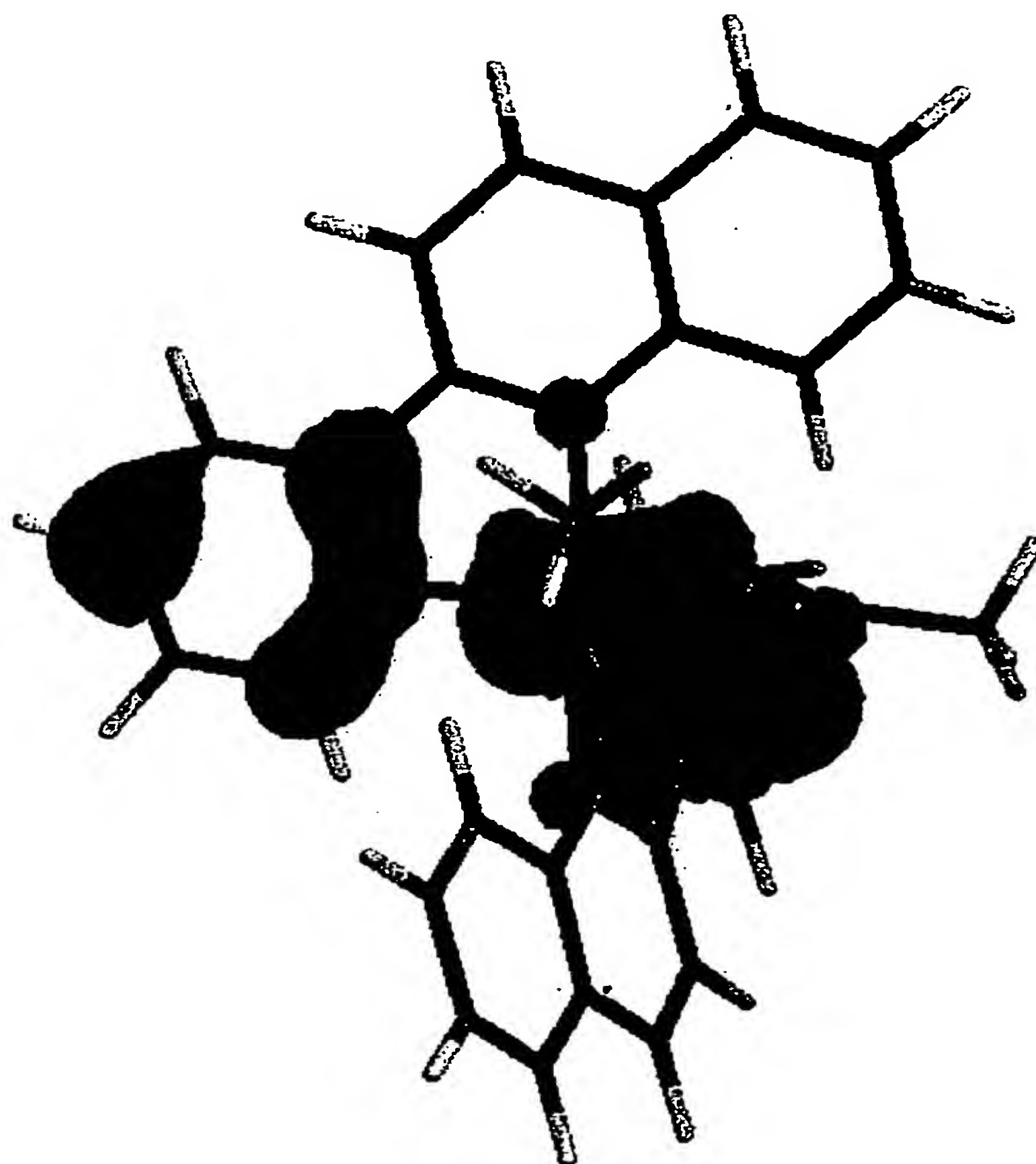
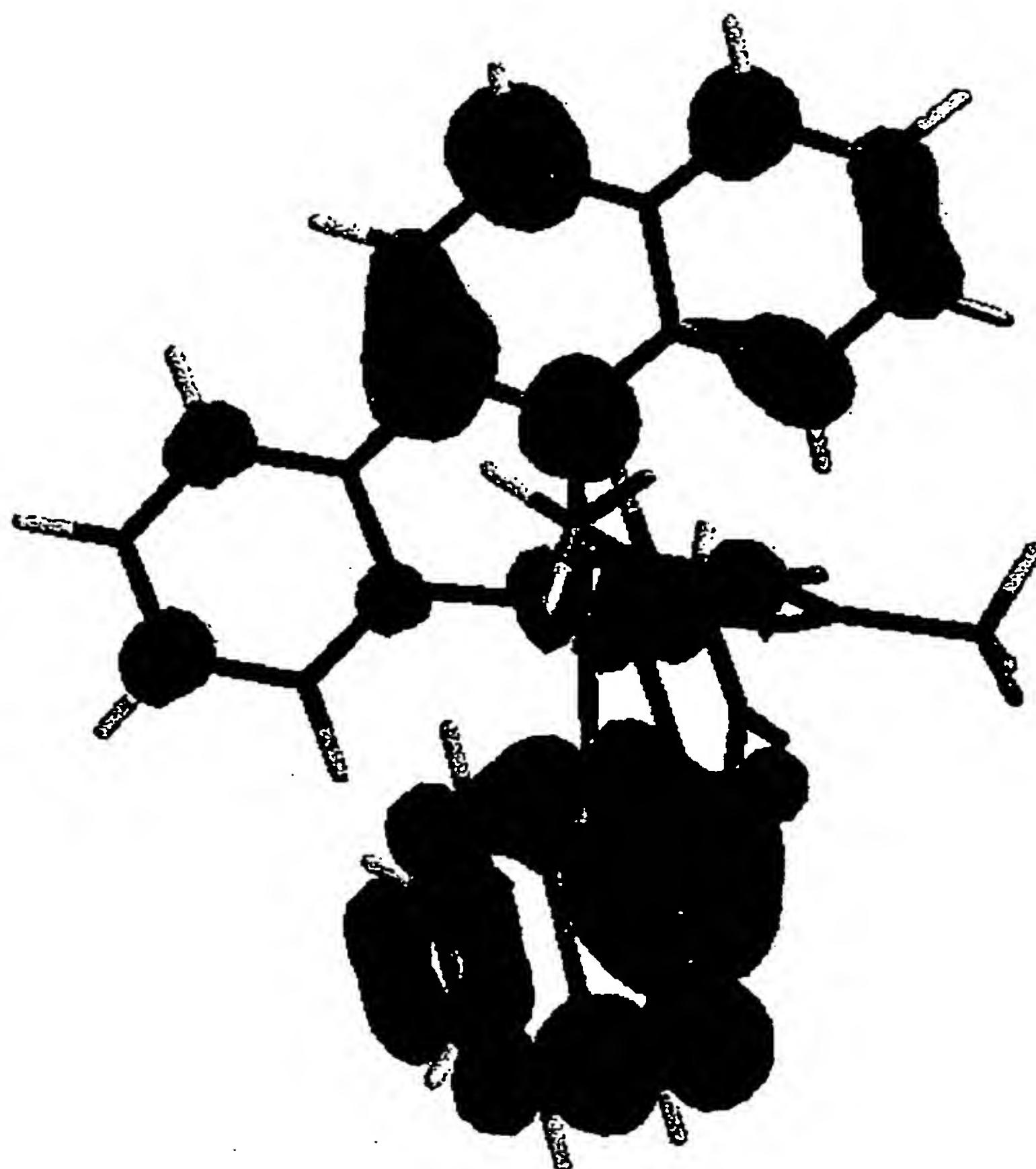


FIGURE 7



HOMO

FIGURE 8



LUMO

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/33040

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 11/06; C07D 215/00, 217/00; H05B 33/14

US CL : 428/690, 917; 313/504; 257/88, 102; 546/4, 10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/690, 917; 313/504; 257/88, 102; 546/4, 10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2001/0019782 A1 (IGARASHI et al) 06 September 2001 (06.09.2001), the whole document, especially, paragraphs [0002], [0025]-[0027], [0085] (with specific reference to formulae (1-8), (1-53), (1-54), (1-56), (1-59) and (1-60)), [0105]-[0125] (with specific reference to formulae (2-2), (2-4), (2-6), (2-7), (2-8), (2-12), (2-13), (2-14), (2-15), (2-18), (2-19) and (2-20)).	1-7, 12-20, 24-28, 36-42, 66-82, 90-96, 98-107, 132, 133, 137 and 138 ----- 8-11, 21-23, 29-35, 43-65, 83-89, 97, 108-131, 134-136 and 139-141

☐ Further documents are listed in the continuation of Box C.

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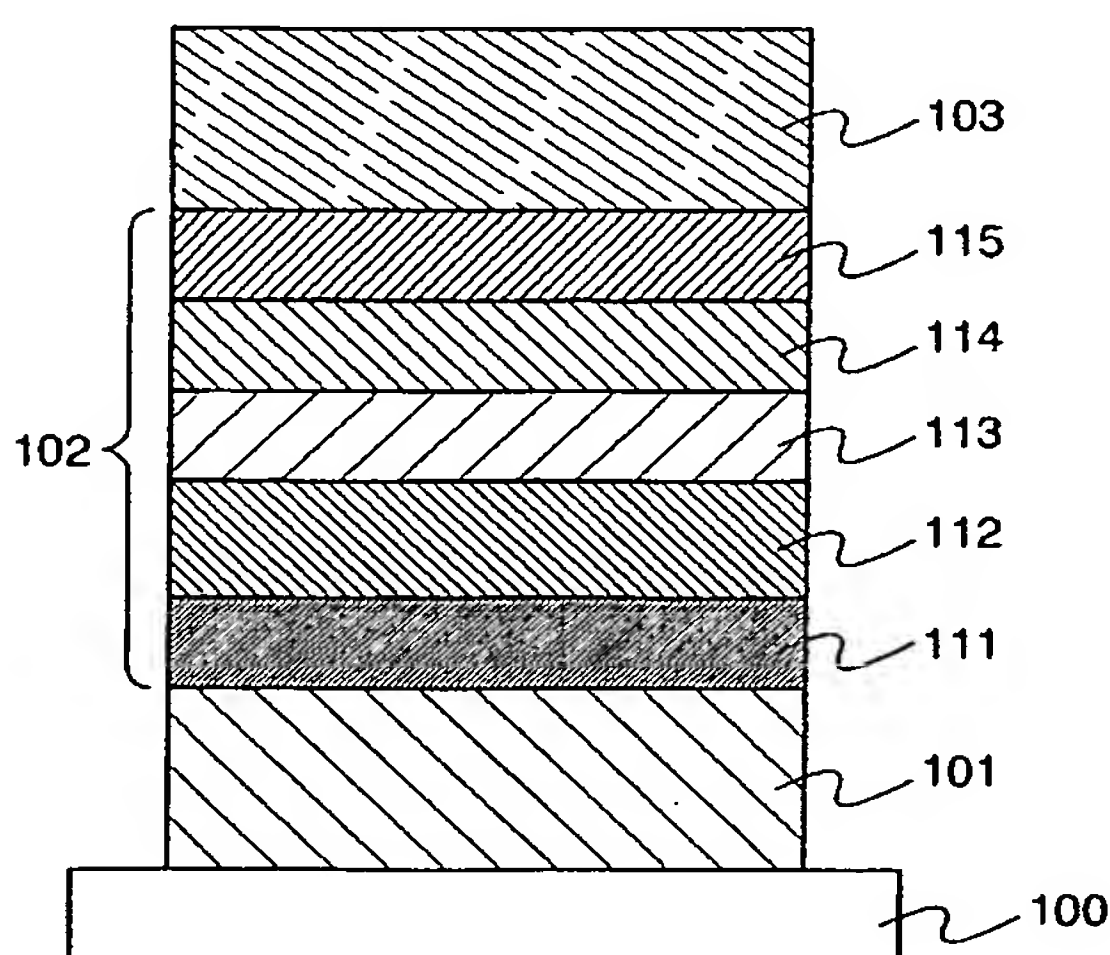
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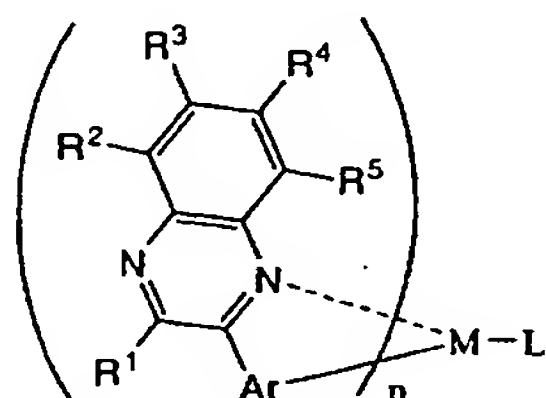
(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,

[Continued on next page]

(54) Title: LIGHT EMITTING ELEMENT AND LIGHT EMITTING DEVICE



(57) Abstract: It is an object of the present invention to obtain an organometallic complex that is capable of converting an excited triplet state into luminescence, a light-emitting element that can be driven for a long time, is high in luminous efficiency, and has a favorable long lifetime, and a light-emitting device using the light-emitting element. The present invention provides a light-emitting element that has a pair of electrodes (an anode and a cathode) and a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex represented by the following general formula (5) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and provides a light-emitting device using the light-emitting device.



(5)



MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION**LIGHT EMITTING ELEMENT
AND
LIGHT EMITTING DEVICE****TECHINICAL FIELD****[0001]**

The present invention relates to an organometallic complex that is capable of converting an excited triplet state into luminescence, a light-emitting element using the organometallic complex, and a light-emitting device using the light-emitting element.

BACKGROUND ART**[0002]**

A light-emitting element using an organic compound is an element in which a layer including an organic compound or an organic compound film emits light by applying an electric field. The emission mechanism is said to be as follows: when a voltage is applied to electrodes with an organic compound film interposed therebetween, an electron injected from a cathode and a hole injected from an anode are recombined in the organic compound film to form a molecular exciton, and energy is released to emit light when the molecular exciton returns to the ground state.

[0003]

In such a light-emitting element, usually, an organic compound layer is formed to be a thin film approximately 1 μm or less. In addition, since such a light-emitting element is an element in which an organic compound itself emits light, a backlight as used for a conventional liquid crystal display is not necessary. Therefore, such a light-emitting element has the big advantage of being able to be manufactured to be thin and lightweight. In addition, for example, in an organic compound film on the order of 100 to 200 nm, the time from injection of carriers to recombination is approximately several tens nanoseconds in consideration of the carrier mobility of the organic

compound film, and light gets to be emitted approximately within microseconds even when the process from the recombination of the carriers to light emission is included. Therefore, it is also one of features that the response speed is quite fast. Further, since such a light-emitting element is a carrier-injection light-emitting element, driving by a direct voltage is possible, and noise is not easily generated. As for the driving voltage, a sufficient luminance of 100 cd/m^2 is achieved at 5.5 V when an organic compound film is a uniform thin film approximately 100 nm in thickness, an electrode material is selected so as to reduce the carrier injection barrier for the organic compound film, and further, a heterostructure (a two-layer structure here) is introduced (for example, refer to Non-Patent Reference 1).

(Non-Patent Reference 1)

C. W. Tang, et al., Applied Physics Letters, vol. 51, No. 12, pp. 913-915 (1987)

[0004]

In addition to such element characteristics such as slimness, lightweight, high-speed response, and direct-current low-voltage driving, it can be also said to be one of big advantages that the luminescent color of a light-emitting element using an organic compound is rich in variation, and the factor is the variety of organic compound themselves. Namely, the flexibility of being able to develop materials for various luminescent colors by molecular design (for example, introduction of a substituent) or the like produces richness of colors. It can be said that the biggest application field of a light-emitting element utilizing this richness of colors is a full-color flat-panel display because there are a lot of organic compounds capable of emitting light's primary colors of red, green, and blue, and thus, full-color images can be achieved easily by patterning of the organic compounds.

[0005]

It can be said that the above-described element characteristics such as slimness, lightweight, high-speed response, and direct-current low-voltage driving are also appropriate characteristics for a flat-panel display. However, in recent years, the use of not fluorescent materials but phosphorescent materials has been tried as an attempt to further improve a luminous efficiency. In the case of a light-emitting element using an

organic compound, luminescence is produced when a molecular exciton returns to the ground state, where the luminescence can be luminescence (fluorescence) from an excited singlet state (S^*) or luminescence (phosphorescence) from an excited triplet state (T^*). When a fluorescent material is used, only luminescence (fluorescence) from S^* contributes.

[0006]

However, it is commonly believed that the statistical generation ratio between S^* and T^* is $S^* : T^* = 1 : 3$ (for example, refer to Non-Patent Reference 2). Accordingly, in the case of a light-emitting element using a fluorescent material, the theoretical limit of the internal quantum efficiency (the ratio of generated photons to injected carriers) is considered to be 25 % on the ground of being $S^* : T^* = 1 : 3$. In other words, in the case of a light-emitting element using a fluorescent material, at least 75 % of injected carriers are wasted uselessly.

(Non-Patent Reference 2)

Tetsuo TSUTSUI, Textbook for the 3rd Workshop, Division of Molecular Electronics and Bioelectronics, Japan Society of Applied Physics, p. 31 (1993)

[0007]

Conversely, it is believed that the luminous efficiency is improved (simply 3 to 4 times) when luminescence from T^* , that is, phosphorescence can be used. However, in the case of a commonly used organic material, luminescence (phosphorescence) from T^* is not observed at room temperature, and normally, only luminescence (fluorescence) from S^* is observed. This is because the ground state of an organic compound is normally a singlet ground state (S_0), and thus, $T^* \rightarrow S_0$ transition is a forbidden transition and $S^* \rightarrow S_0$ transition is an allowed transition. In reality, in recent years, light-emitting elements in which energy (hereinafter, referred to as "triplet excitation energy") that is emitted on returning from T^* to a ground state can be converted into luminescence have been released one after another (for example, refer to Non-Patent Reference 3).

(Non-Patent Reference 3)

Tetsuo TSUTSUI, et al., Japanese Journal of Applied Physics, vol. 38, pp. L1502-L1504

(1999)

[0008]

In Non-Patent Reference 3, a metal complex including iridium as a central metal (hereinafter, referred to as "iridium complex") is used as a luminescent material, and it can be said to be a feature that an element of the third transition series is introduced as a central metal. This metal complex is a material (hereinafter, referred to as "triplet luminescent material") capable of converting an excited triplet state into luminescence at room temperature. As described in Non-Patent Document 3, a light-emitting element using an organic compound capable of converting triplet excitation energy into luminescence can achieve a higher internal quantum efficiency than ever before. Further, when the higher internal quantum efficiency can be achieved, the luminous efficiency (lm/W) is also improved.

[0009]

However, according to the report of Non-Patent Reference 3, the half-life of luminance is approximately 170 hours when the initial luminance is controlled to be 500 cd/m² in constant current driving, and so, a light-emitting element using a triplet luminescent material has a problem with the lifetime. On the other hand, in the case of a light-emitting element using a singlet luminescent material, the half-life of luminance reaches several to ten thousands hours when the initial luminance is controlled to be 500 cd/m² in constant current driving, and so, it can be said that the light-emitting element has a practical use in terms of the lifetime.

[0010]

Accordingly, in a light-emitting element using a triplet luminescent material, an element that can be driven for a long time is desired. This is because a light-emitting element that is high in luminous efficiency and has a long lifetime can be obtained.

DISCLOSURE OF INVENTION

[0011]

In view of the technical background related to light-emitting elements, it is an object of the present invention to solve the problem in related art. It is an object of the

present invention to provide a material capable of emitting phosphorescence. In a light-emitting element using an organometallic complex capable of converting an excited triplet state into luminescence, it is an object of the present invention to provide a light-emitting element that can be driven for a long time, that is, that is high in luminous efficiency and has a long lifetime. Further, it is an object of the present invention to provide a light-emitting device that can be driven for a long time with low power consumption by using the light-emitting element.

[0012]

A lot of earnest experiments and studies by the inventors to achieve the object have finally found out that an organometallic complex including a structure represented by any one of the following general formulas (1) to (4) is capable of emitting phosphorescence and that an organometallic complex represented by any one of the following general formulas (5) to (8) is capable of emitting phosphorescence to come to complete the invention.

[0013]

A lot of earnest experiments and studies by the inventors to achieve the object have finally found out that, in a light-emitting element formed by providing a pair of electrodes (an anode and a cathode) and at least one layer including an organic compound between the pair of electrodes, a light-emitting element that can be driven for a long time, that is, that is high in luminous efficiency and has a long lifetime can be obtained when a specific compound is included in at least one layer of the layer including the organic compound to come to complete the invention.

[0014]

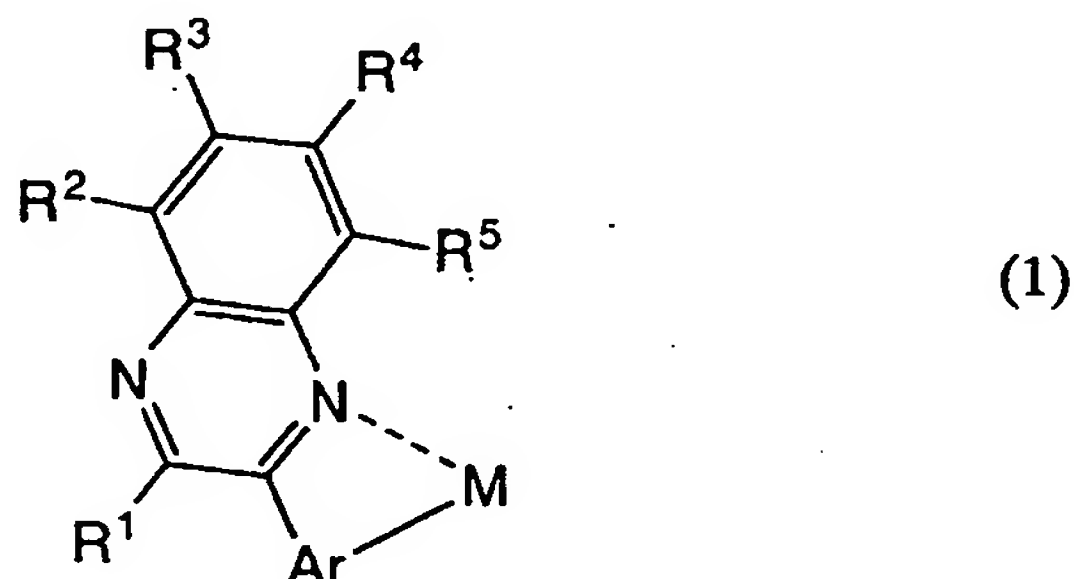
A lot of earnest experiments and studies by the inventors to achieve the object have finally completed a light-emitting device that can be driven for a long time with low power consumption by using the light-emitting element.

[0015]

Organometallic complexes, light-emitting elements, and light-emitting devices according to the present invention will be described below in sequence.

[0016]

One of organometallic complexes according to the present invention is an organometallic complex including a structure represented by the following general formula (1).



10 [0017]

In the formula (1), R^1 to R^5 are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10. It is preferable that Ar be one of an aryl group having an electron-withdrawing group and a heterocyclic group having electron-withdrawing group. When Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having electron-withdrawing group, phosphorescence with larger emission intensity can be emitted.

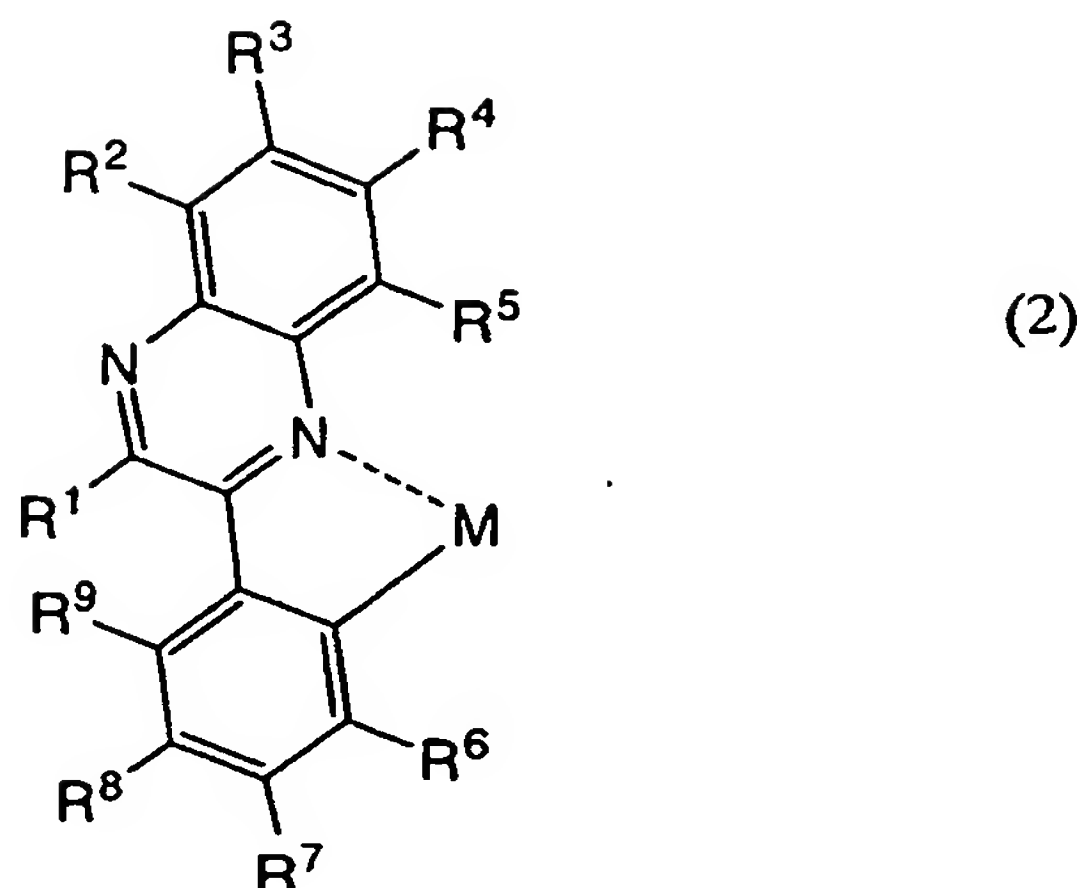
20 [0018]

Further, a first light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex including a structure represented by the general formula (1) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0019]

One of organometallic complexes according to the present invention is an organometallic complex including a structure represented by the following general formula (2).

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10 [0020]

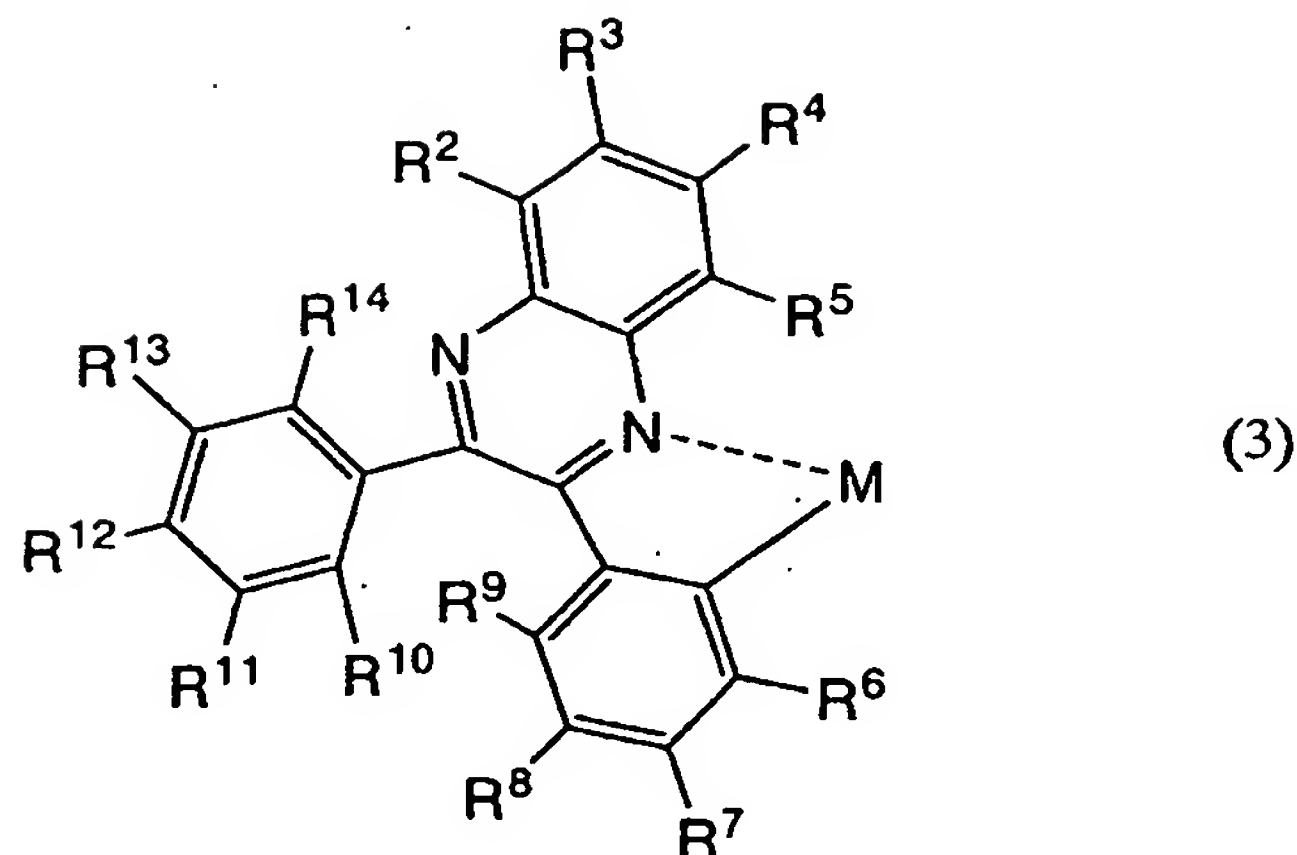
In the formula (2), R^1 to R^9 are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, and a heterocyclic group, at least one of R^6 to R^9 is an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10. When at least one of R^6 to R^9 is an electron-withdrawing group, phosphorescence with larger emission intensity can be emitted.

[0021]

Further, a second light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex including a structure represented by the general formula (2) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0022]

One of organometallic complexes according to the present invention is an organometallic complex including a structure represented by the following general formula (3).



10 [0023]

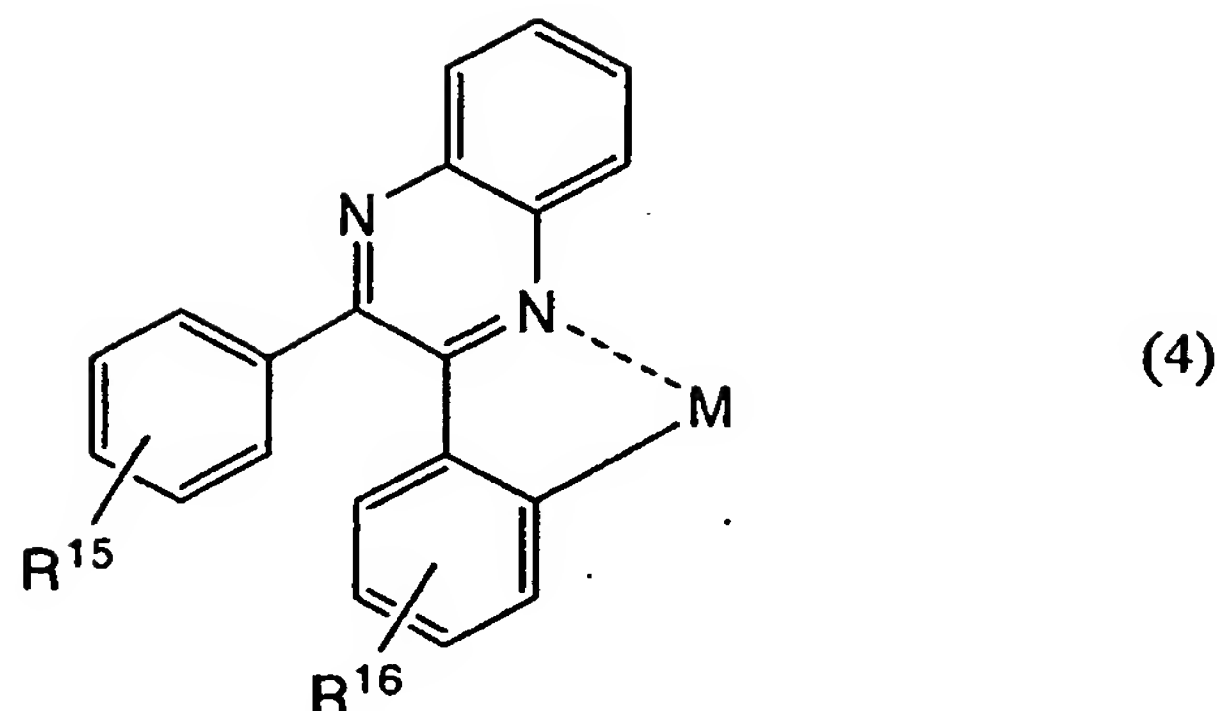
In the formula (3), R^2 to R^{14} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10. It is preferable that at least one of R^6 to R^9 be an electron-withdrawing group. This makes it possible to emit phosphorescence with larger emission intensity.

[0024]

Further, a third light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex including a structure represented by the general formula (3) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0025]

One of organometallic complexes according to the present invention is an organometallic complex including a structure represented by the following general formula (4).



[0026]

10 In the formula (4), R^{15} and R^{16} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10. It is preferable that R^{16} be an electron-withdrawing group. This makes it possible to emit phosphorescence with larger emission intensity.

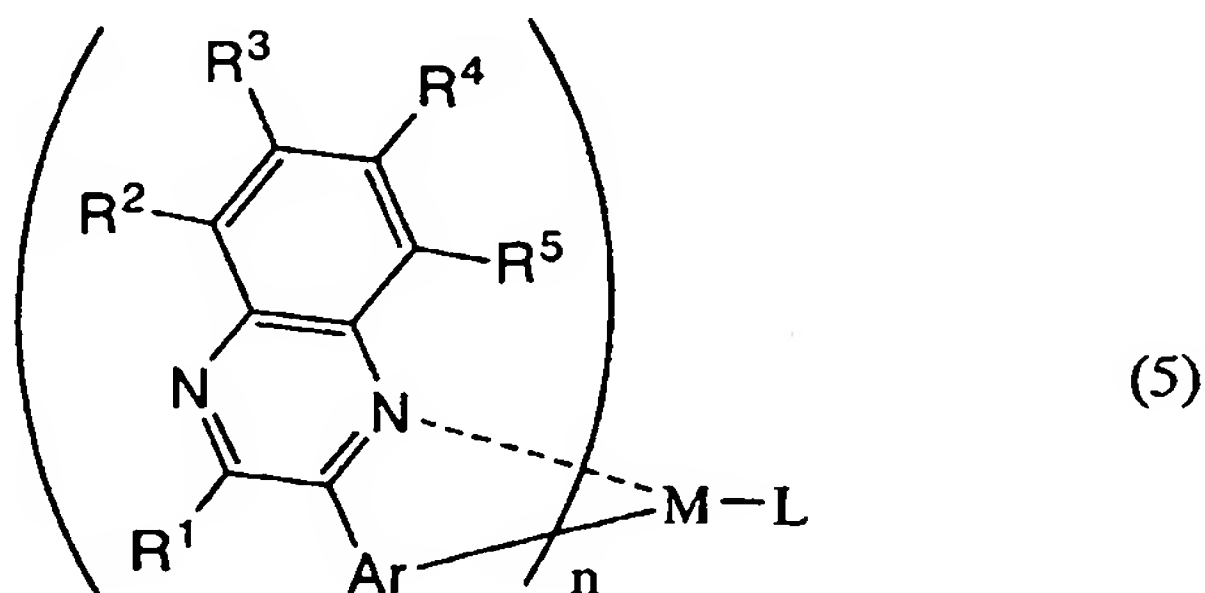
[0027]

15 Further, a fourth light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex including a structure represented by the general formula (4) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

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[0028]

One of organometallic complexes according to the present invention is an organometallic complex represented by the following general formula (5).



[0029]

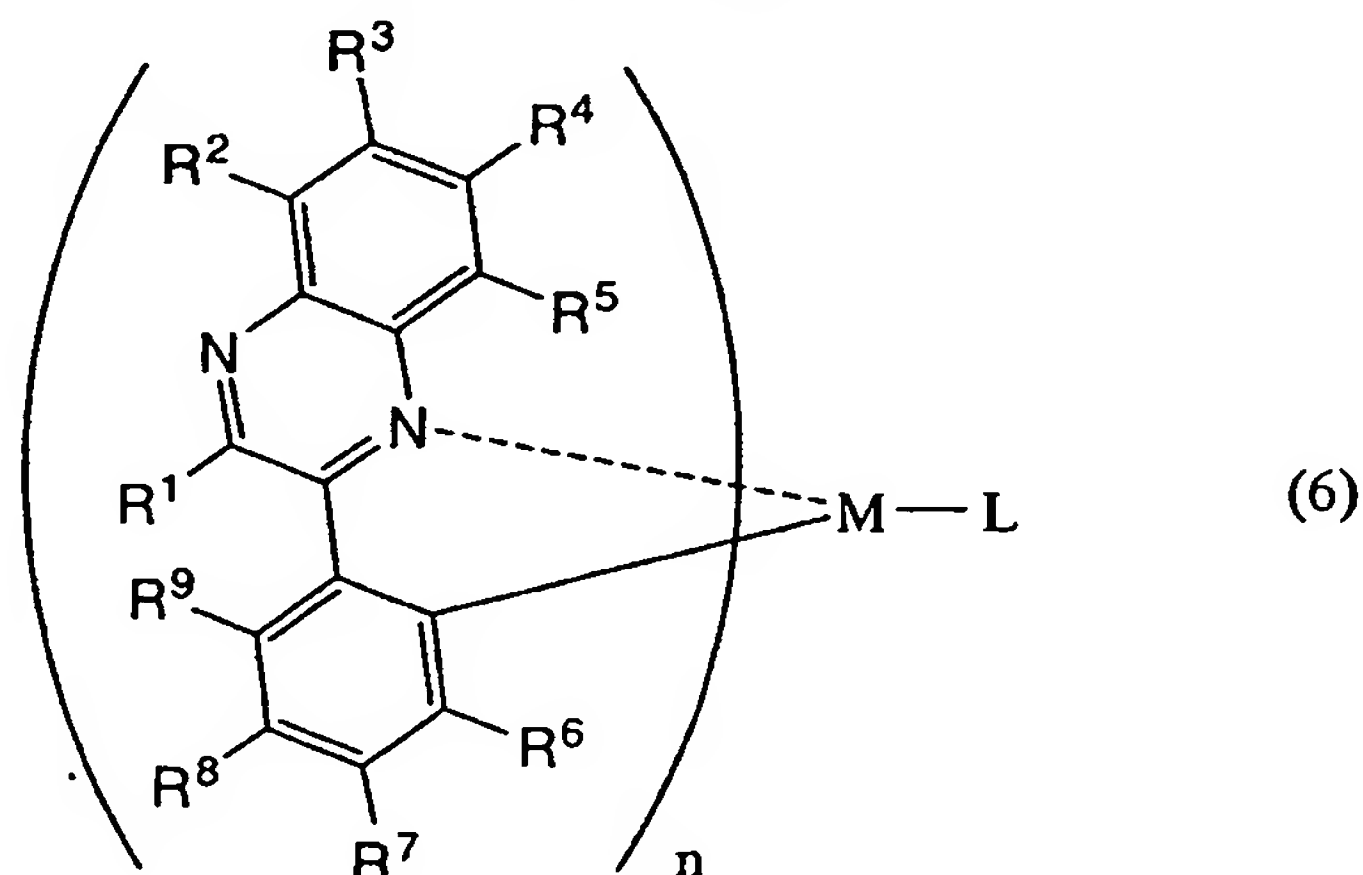
In the formula (5), R^1 to R^5 are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is a monoanionic ligand. When Ar is an electron-withdrawing group, phosphorescence with larger emission intensity can be emitted.

[0030]

Further, a fifth light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex represented by the general formula (5) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0031]

One of organometallic complexes according to the present invention is an organometallic complex represented by the following general formula (6).



[0032]

In the formula (6), R^1 to R^5 are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, R^6 to R^9 are individually any one selected from the group consisting of hydrogen, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a heterocyclic group, and an electron-withdrawing group, it is preferable that at least one of R^6 to R^9 be an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is any one of a monoanionic ligand having a β -diketone structure, a monoanionic bidentate ligand having a carboxyl group, and a monoanionic bidentate ligand having a phenolic hydroxyl group. When at least one of R^6 to R^9 is an electron-withdrawing group, phosphorescence with larger emission intensity can be emitted.

The present invention provides organometallic complexes represented by the general formula (6) unless R^1 to R^9 are individually hydrogen and the anionic ligand L is an acetylacetone anion, or at least one of R^6 to R^9 is not an electron-withdrawing group.

[0033]

Further, a sixth light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex represented by the general formula (6) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0034]

It is to be noted that a compound is shown as "(1-70)" in the [0086] paragraph of Japanese Patent Application Laid-Open No. 2001-247859, and the compound corresponds to an organometallic complex represented by the general formula (6), where R^1 to R^9 are all individually hydrogen, M is iridium, n is 2, and anionic ligand L corresponds to acetylacetone anion. However, in the compound, any of R^6 to R^9 is not an electron-withdrawing group, but hydrogen. In addition, a synthesis method, a

property, or the like of the compound is not disclosed anywhere in Japanese Patent Application Laid-Open No. 2001-247859. On the other hand, the compound is not included in organometallic complexes represented by the general formula (6) according to the present invention, and a compound in which R^1 to R^9 are individually hydrogen and the anionic ligand L is an acetylacetonate anion or a compound in which R^6 to R^9 are all individually hydrogen without having an electron-withdrawing group is not included in organometallic complexes represented by the general formula (6) according to the present invention.

[0035]

10 (Patent Reference 1)

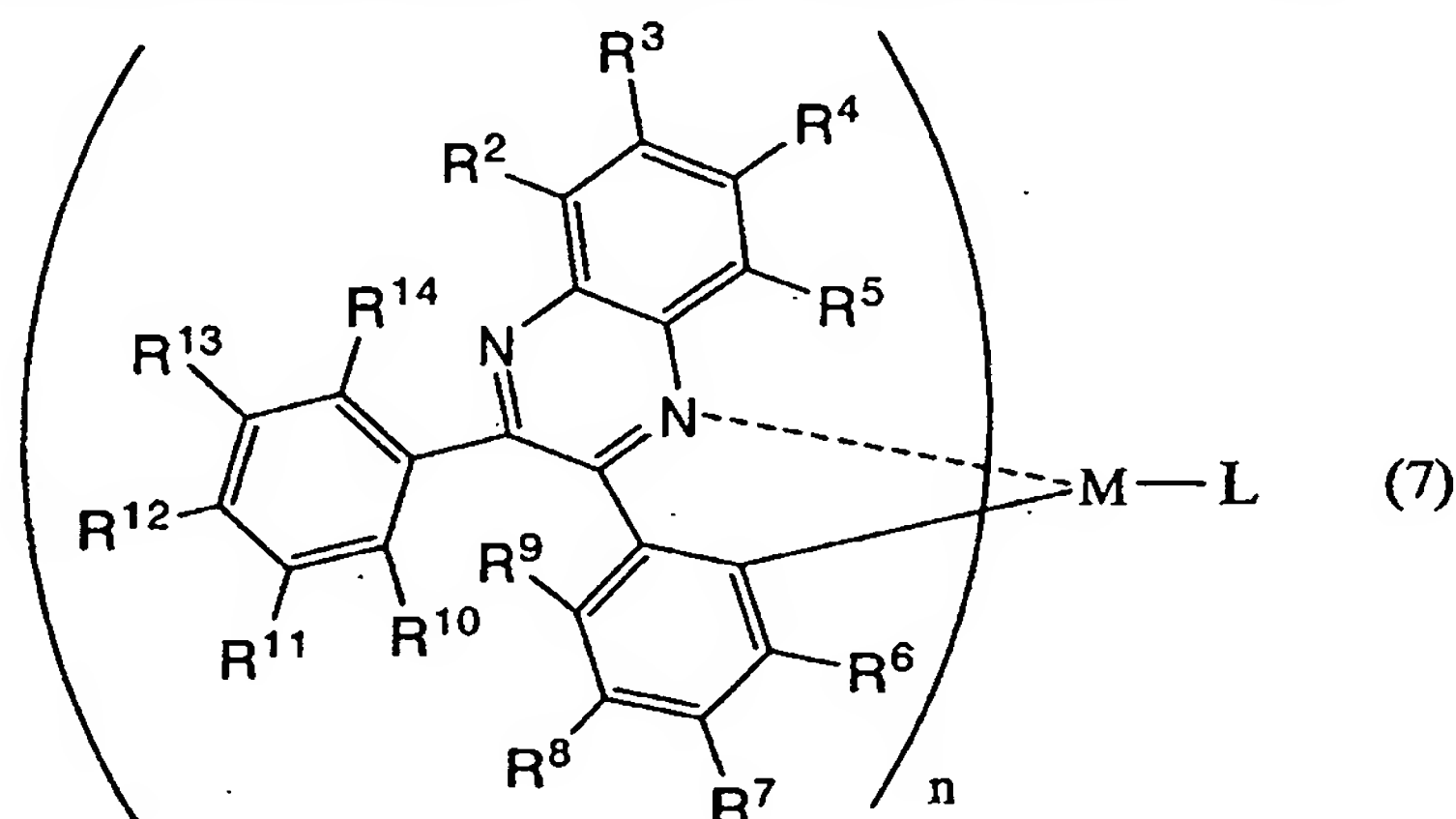
Japanese Patent Application Laid-Open No. 2001-247859

[0036]

One of organometallic complexes according to the present invention is an organometallic complex represented by the following general formula (7).

15

20



[0037]

In the formula (7), R^2 to R^{14} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand. Here, it is preferable that at least one of R^6 to R^9 be an electron-withdrawing group. This makes it possible to emit phosphorescence with

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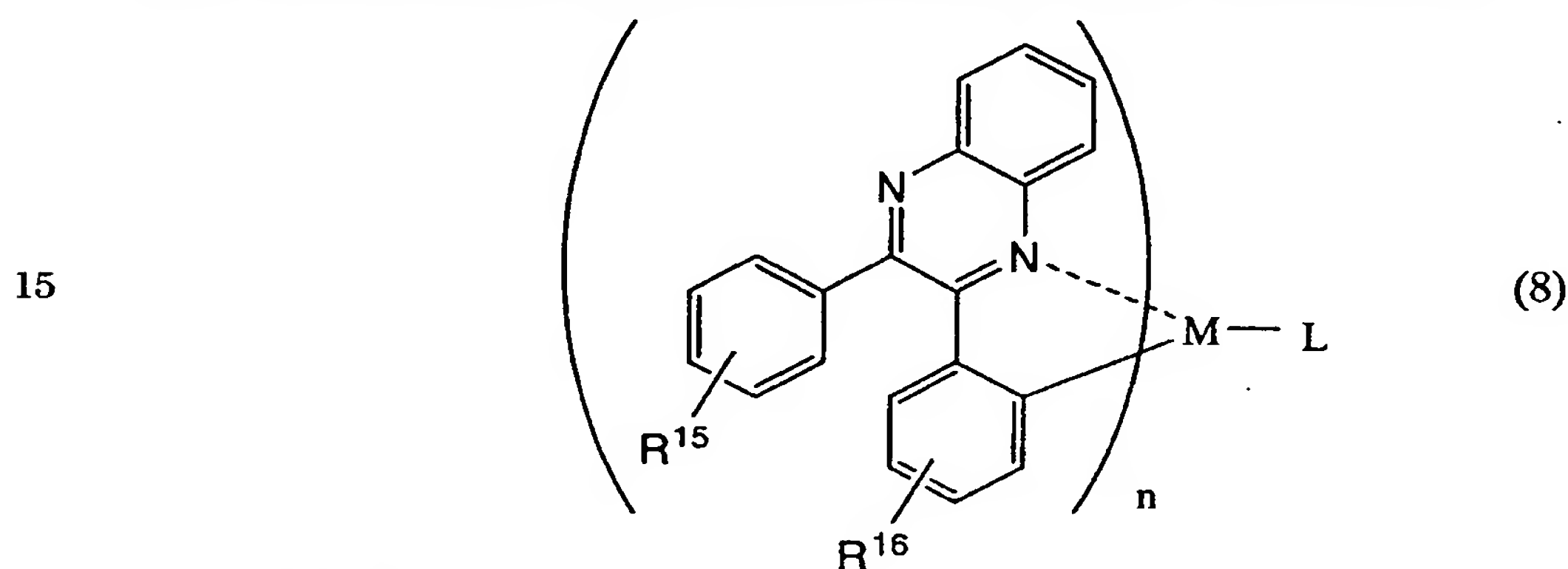
larger emission intensity.

[0038]

Further, a seventh light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where the light-emitting layer includes an organometallic complex represented by the general formula (7) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

[0039]

One of organometallic complexes according to the present invention is an organometallic complex represented by the following general formula (8).



[0040]

20 In the formula (8), R^{15} and R^{16} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand. Here, it is preferable that at least one of R^{16} be an electron-withdrawing group. This makes it possible to emit phosphorescence with larger emission intensity.

[0041]

30 Further, a eighth light-emitting element according to the present invention is a light-emitting element that has a light-emitting layer between a pair of electrodes, where

the light-emitting layer includes an organometallic complex represented by the general formula (8) and one of a compound that has a larger energy gap than the organometallic complex and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex.

5 [0042]

Here, in the organometallic complex including the structure represented by the general formula (3) or (4), or the organometallic complex represented by the general formula (7) or (8), it is preferable that the electron-withdrawing group be any one of a halogen group, a haloalkyl group, and a cyano group. This improves the chromaticity and quantum efficiency of the organometallic complex. In addition, a fluoro group is particularly preferable as the halogen group, and a trifluoromethyl group is particularly preferable as the haloalkyl group. This improves also the electron trap efficiency.

[0043]

15 In the organometallic complex represented by the general formula (7) or (8), it is preferable that the central metal M be a heavy metal, particularly, iridium or platinum. This makes it possible to obtain a heavy atom effect.

[0044]

A ninth light-emitting element according to the present invention is any one of the first to eighth light-emitting elements, where the compound that has the larger energy gap than the organometallic complex is one of 4, 4' - bis [N - (1 - naphthyl) - N - phenylamino] - biphenyl and tris (8 - quinolinolato) aluminum.

[0045]

25 A tenth light-emitting element according to the present invention is any one of the fifth to eighth light-emitting elements, where the anionic ligand L is one of a monoanionic ligand having a β -diketone structure, a monoanionic bidentate ligand having a carboxyl group, and a monoanionic bidentate ligand having a phenolic hydroxyl group.

[0046]

30 An eleventh light-emitting element according to the present invention is any one of the first to eighth light-emitting elements, where the light-emitting layer includes

the organometallic complex, a first compound that has a larger energy gap than the organometallic complex and has an electron mobility of 10^{-6} cm²/Vs or more, and/or a second compound that has a larger energy gap than the organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or more.

5 [0047]

A twelfth light-emitting element according to the present invention is any one of the first to eighth light-emitting elements, where the light-emitting layer includes the organometallic complex, a first compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has an electron mobility
10 of 10^{-6} cm²/Vs or more, and/or a second compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or more.

[0048]

A thirteenth light-emitting element according to the present invention is the
15 eleventh or twelfth light-emitting element, where a hole transporting compound is an aromatic amine compound, and an electron transporting compound is a metal complex.

[0049]

A fourteenth light-emitting element according to the present invention is any one of the first to thirteenth light-emitting element, which further has at least one of a
20 hole injecting layer, a hole transporting layer, a hole blocking layer, an electron transporting layer, and an electron injecting layer.

[0050]

In addition, a light-emitting device according to the present invention is a light-emitting device manufactured by using any one of the first to fourteenth
25 light-emitting elements.

[0051]

According to the present invention, an organometallic complex that is capable of emitting phosphorescence can be obtained. In addition, a light-emitting element that has a light-emitting layer including the organometallic complex and a compound
30 that has a larger energy gap than the organometallic complex can be driven for a long

time, is high in luminous efficiency, and has a long lifetime. By using the organometallic complex according to the present invention as a luminescent material, a light-emitting element that is capable of providing red or reddish luminescence that is excellent in chromaticity can be obtained.

5 [0052]

In addition, a light-emitting element that is capable of emitting light efficiently can be obtained by using the organometallic complex according to the present invention as a sensitizer. Further, by using an organometallic complex into which an electron-withdrawing group is introduced in particular among organometallic
10 complexes according to the present invention, a light-emitting element that is excellent in recombination efficiency can be obtained.

[0053]

Moreover, a light-emitting device according to the present invention has excellent performance due to the use of the light-emitting element.

15

BRIEF DESCRIPTION OF DRAWINGS

In the accompanying drawings:

FIG. 1 is a diagram illustrating the structure of a light-emitting element according to the present invention;

20 FIG. 2 is a diagram illustrating the structure of a light-emitting element according to the present invention;

FIG. 3 is a diagram illustrating a light-emitting device;

FIG. 4 is a diagram illustrating Embodiment mode mode 4 of the present invention;

25 FIG. 5 is a diagram illustrating Embodiment mode mode 5 of the present invention;

FIG. 6 is a diagram illustrating Embodiment mode mode 5 of the present invention;

30 FIG. 7 is a diagram illustrating Embodiment mode mode 6 of the present invention;

FIG. 8 is a diagram illustrating Embodiment mode mode 7 of the present invention;

FIG. 9 is a diagram illustrating Embodiment mode mode 7 of the present invention;

5 FIG. 10 is a diagram illustrating Embodiment mode mode 7 of the present invention;

FIG. 11 is a diagram illustrating Embodiment mode mode 7 of the present invention;

10 FIGS. 12A to 12C are diagrams illustrating Embodiment mode mode 8 of the present invention;

FIG. 13 is a diagram showing an absorption spectrum and an emission spectrum of an organometallic complex obtained in Synthesis Example 1 of Embodiment 1;

15 FIG. 14 is a diagram showing an absorption spectrum and an emission spectrum of an organometallic complex obtained in Synthesis Example 2 of Embodiment 1;

FIG. 15 is a diagram showing an absorption spectrum and an emission spectrum of an organometallic complex obtained in Synthesis Example 3 of Embodiment 1;

20 FIG. 16 is a diagram showing an absorption spectrum and an emission spectrum of an organometallic complex obtained in Synthesis Example 4 of Embodiment 1;

FIG. 17 is a diagram showing an absorption spectrum and an emission spectrum of an organometallic complex obtained in Synthesis Example 5 of Embodiment 1;

FIGS. 18A and 18B are diagrams showing CV curves respectively in the case of examining oxidation characteristics and reduction characteristics of the organometallic complex $[\text{Ir}(\text{Fdpq})_2(\text{acac})]$ in Synthesis Example 1;

30 FIG. 19 is a diagram illustrating the structure of a light-emitting element in Embodiment 2 and a manufacturing method thereof;

FIGS. 20A to 20C are diagrams showing initial characteristics of the light-emitting element manufactured in Embodiment 2;

FIG. 21 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 2;

5 FIG. 22 is a diagram illustrating the structure of a light-emitting element in Embodiment 3 and a manufacturing method thereof;

FIGS. 23A to 23C are diagrams showing initial characteristics of the light-emitting element manufactured in Embodiment 3;

10 FIG. 24 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 3;

FIGS. 25A to 25C are diagrams showing initial characteristics of a light-emitting element manufactured in Embodiment 4;

FIG. 26 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 4;

15 FIGS. 27A to 27C are diagrams showing operation characteristics of a light-emitting element manufactured in Embodiment 5;

FIG. 28 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 5;

20 FIGS. 29A to 29C are diagrams showing operation characteristics of a light-emitting element manufactured in Embodiment 6;

FIG. 30 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 6;

FIGS. 31A to 31C are diagrams showing operation characteristics of a light-emitting element manufactured in Embodiment 7;

25 FIG. 32 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 7;

FIGS. 33A to 33C are diagrams showing operation characteristics of a light-emitting element manufactured in Embodiment 8

30 FIG. 34 is a diagram showing the result of an operational stability test for the light-emitting element manufactured in Embodiment 8;

FIGS. 35A and 35B are diagrams illustrating a light-emitting device (Embodiment 9) that has a light-emitting element according to the present invention in a pixel portion;

FIGS. 36A to 36E are diagrams illustrating specific examples of electronic devices to which the present invention is applied (Embodiment 10);

FIG. 37 is a diagram illustrating a structure example of a white light-emitting element (Embodiment 11);

FIG. 38 is a diagram illustrating the structure of a white light-emitting element using a phosphorescent material, which is different from the structure in Embodiment 11 (Embodiment 12);

FIG. 39 is a diagram illustrating a light-emitting element using an organometallic complex as a luminescent material and a manufacturing method thereof (Embodiment 13);

FIG. 40 is a diagram showing an emission spectrum of the light-emitting element in Embodiment 13;

FIG. 41 is a diagram showing a ^1H -NMR chart of TPAQn used in Embodiment 13;

FIG. 42 is a diagram illustrating a light-emitting element using the organometallic complex synthesized in Synthesis Example 3 as a luminescent material and a manufacturing method thereof (Embodiment 14);

FIG. 43 is a diagram showing an emission spectrum of the light-emitting element manufactured in Embodiment 14;

FIG. 44 is a diagram showing an emission spectrum of the light-emitting element manufactured in Embodiment 15;

FIG. 45 is a diagram showing an emission spectrum of the light-emitting element manufactured in Embodiment 16; and

FIG. 46 is a diagram showing an emission spectrum of the light-emitting element manufactured in Embodiment 17.

BEST MODE FOR CARRYING OUT THE INVENTION

[0054]

The present invention will be described in more detail below. First, organometallic complexes according to the present invention will be described. The present invention provides a novel organometallic complex, a light-emitting element using the organometallic complex, and a light-emitting device using the light-emitting element.

[0055]

Specific examples of the substituents R^1 to R^{16} described above are as follows.

10 The acyl group includes an acetyl group, a propionyl group, an isobutyryl group, and a methacryloyl group. The alkyl group includes a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, a tert-butyl group, and an octyl group. The alkoxyl group includes a methoxy group, an ethoxy group, and a propoxy group. The aryl group includes a phenyl group, a 4-methylphenyl group and a 4-ethylphenyl group.

15 The heterocyclic group includes a pyridyl group, bipyridyl group, and a methylpyridyl group. The electron-withdrawing group includes a fluoro group, a trifluoro group, and a cyano group.

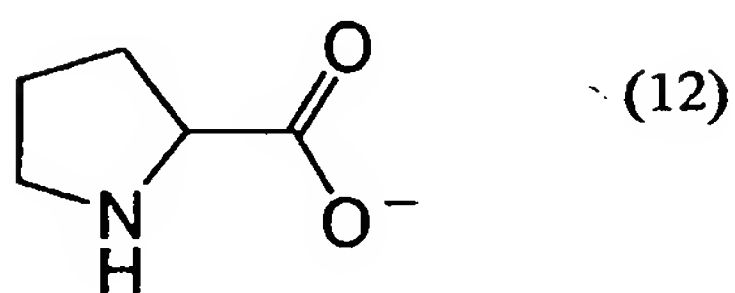
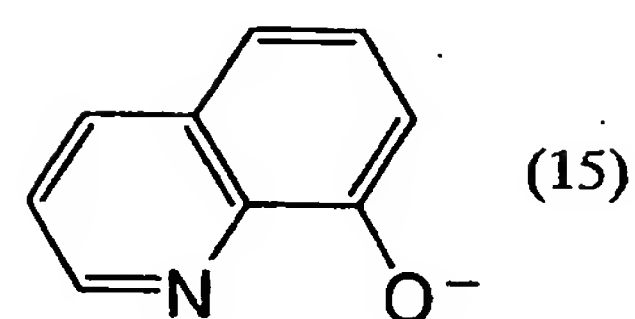
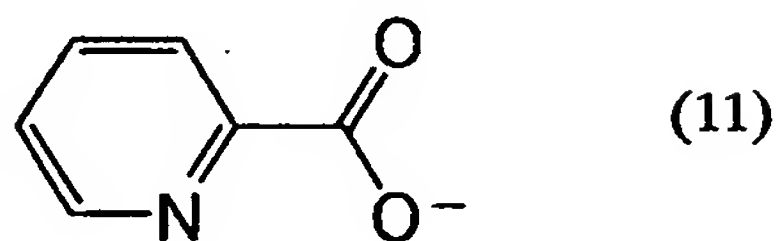
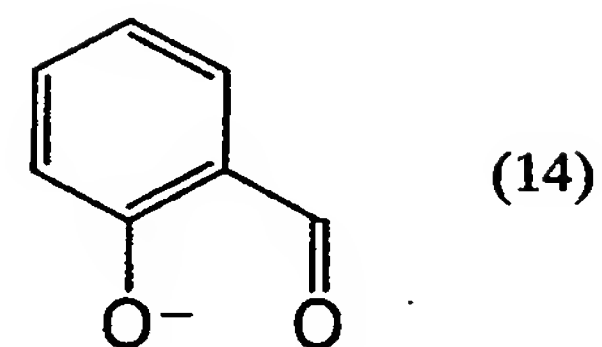
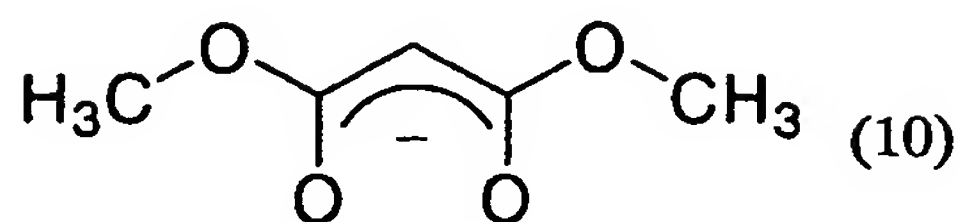
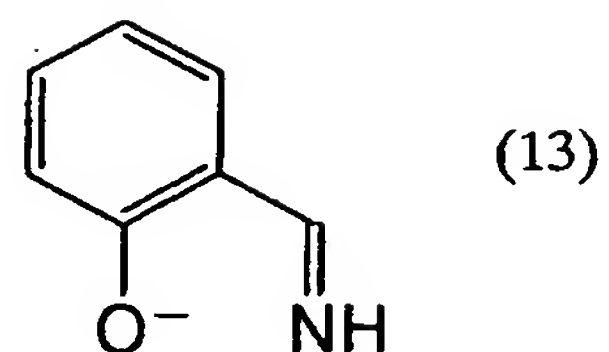
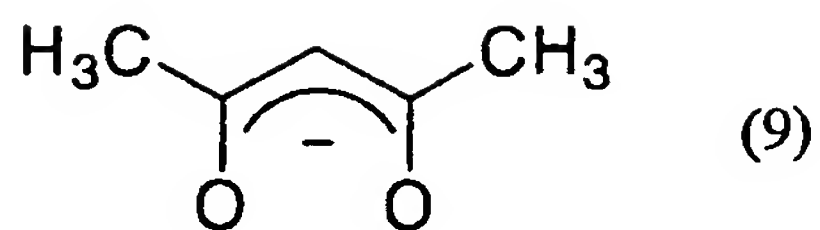
[0056]

In addition, specific examples of the element of Group 9 or the element of Group 10 include iridium and platinum. However, the element of Group 9 or the element of Group 10 is not to be considered limited to these elements given as examples.

[0057]

Then, the ligand L is any one of a monoanionic ligand having a β -diketone structure, a monoanionic bidentate ligand having a carboxyl group, and a monoanionic bidentate ligand having a phenolic hydroxyl group. Specific examples thereof include anions represented by the following formulas (9) to (15). These ligands are effective in that they have high coordination ability and are inexpensively available.

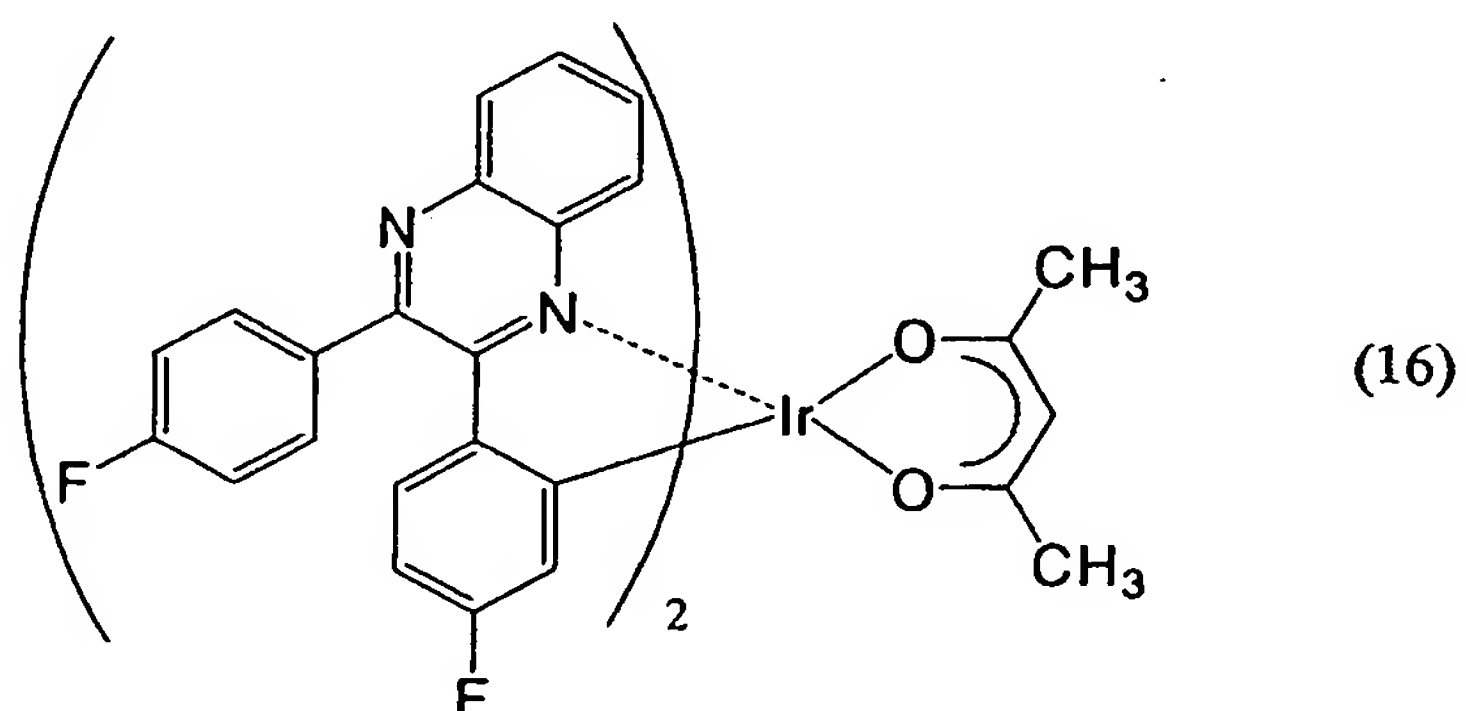
[0058]



[0059]

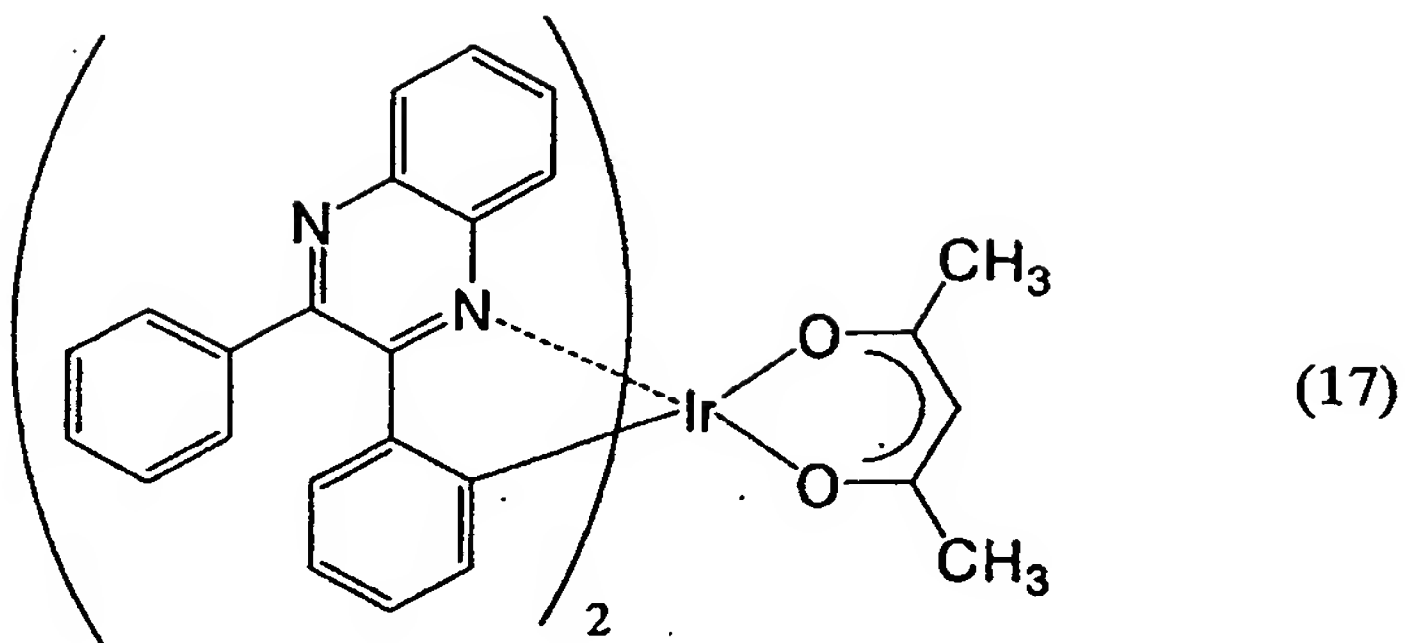
Typical examples of organometallic complexes including a structure represented by one of the general formulas (1) to (4), that is, organometallic complexes represented by the general formulas (5) to (8) are given below. However, the organometallic complexes are not to be considered limited to these compounds.

[0060]



[0061]

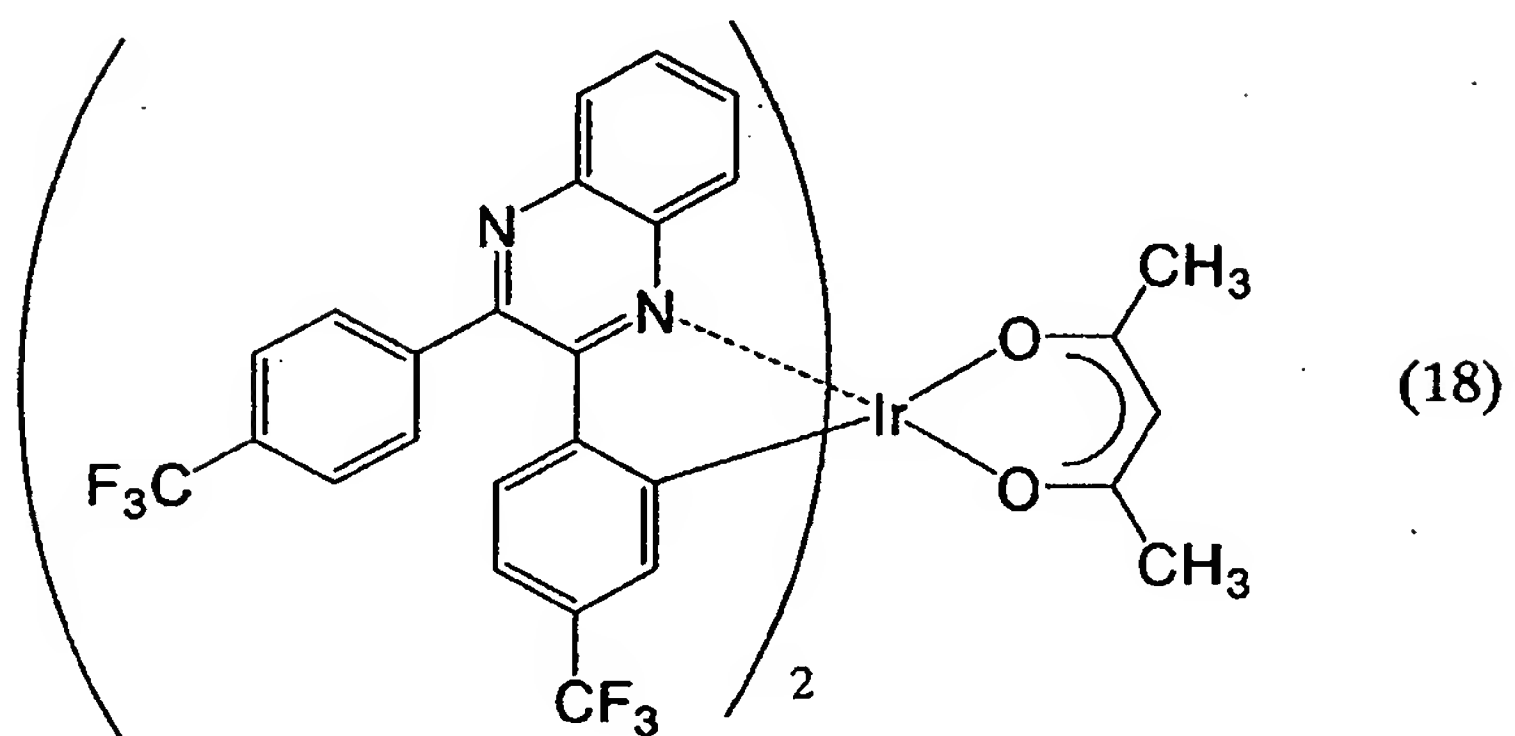
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[0062]

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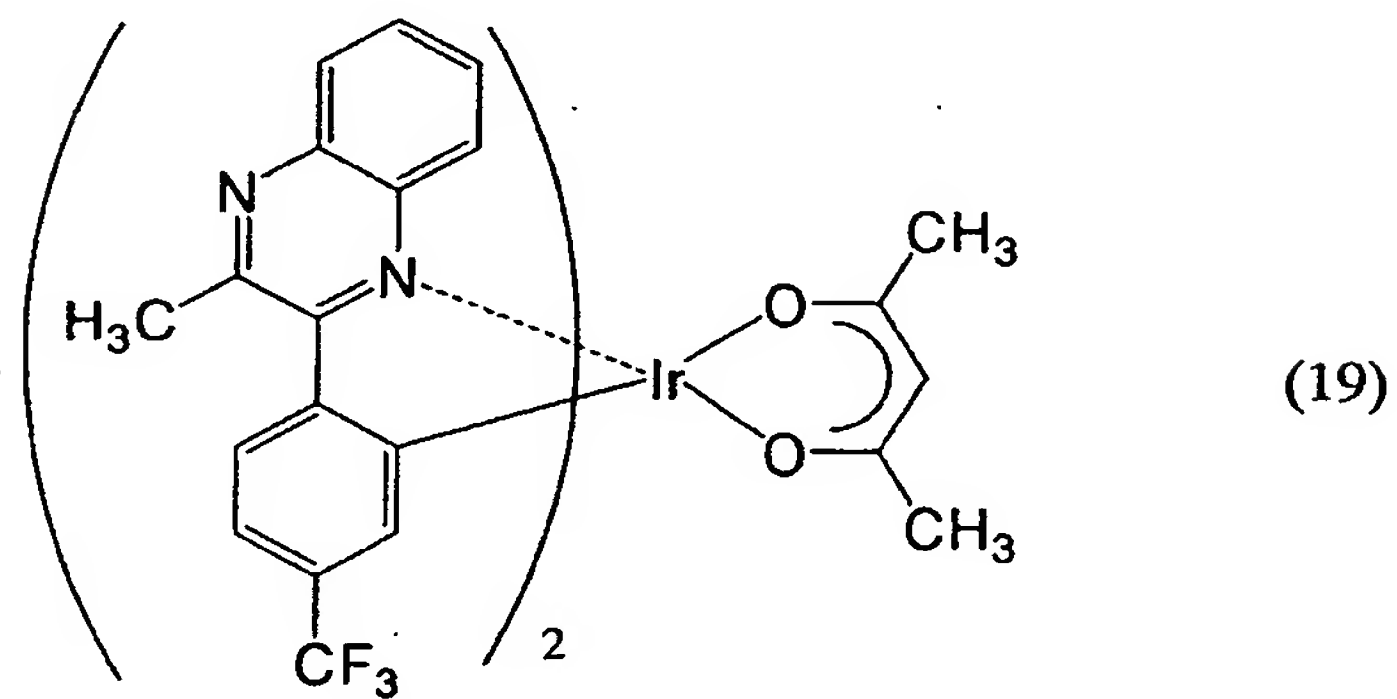
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[0063]

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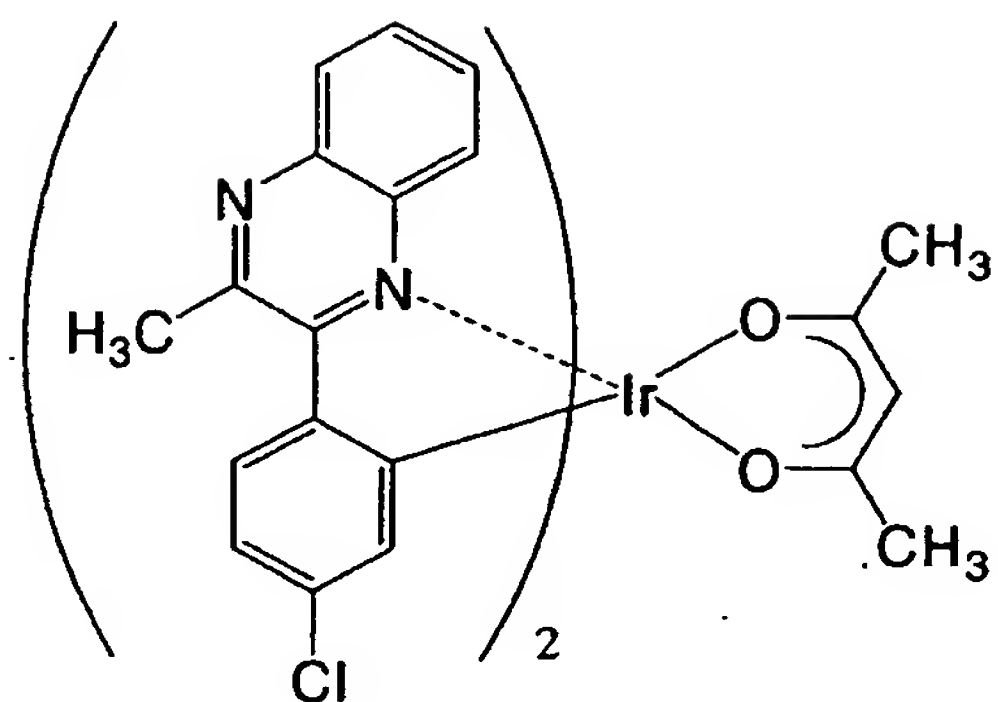
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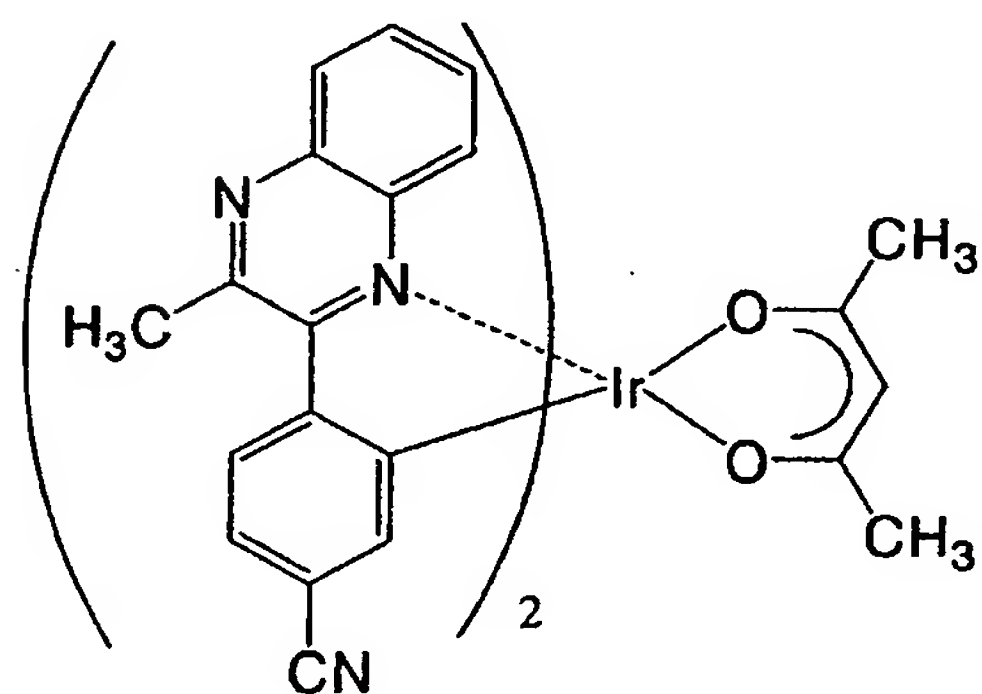
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[0064]



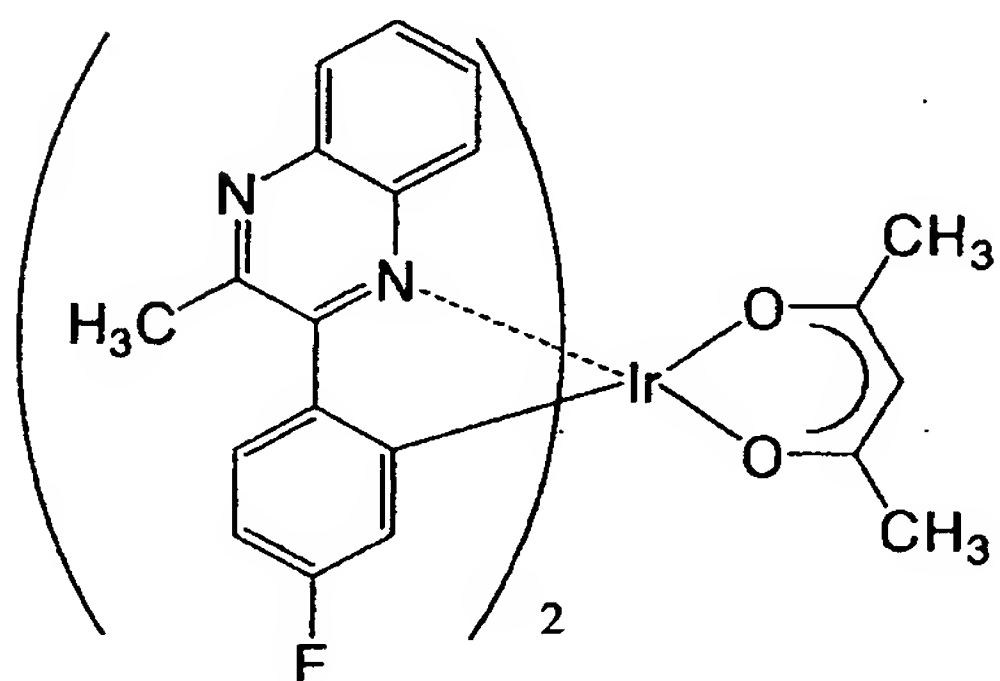
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[0065]



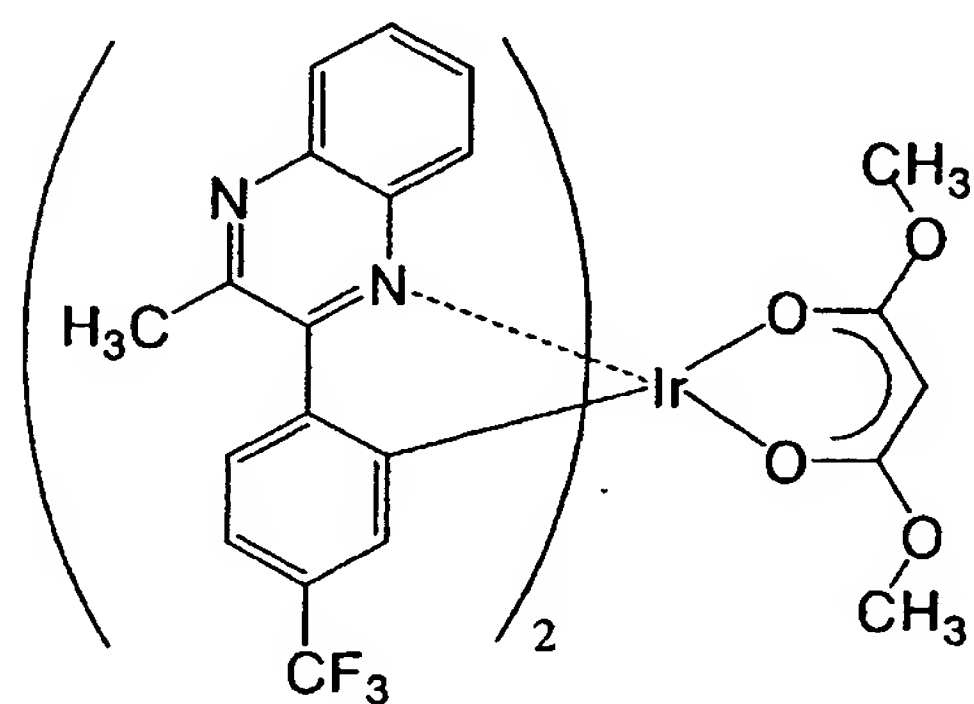
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[0066]



(22)

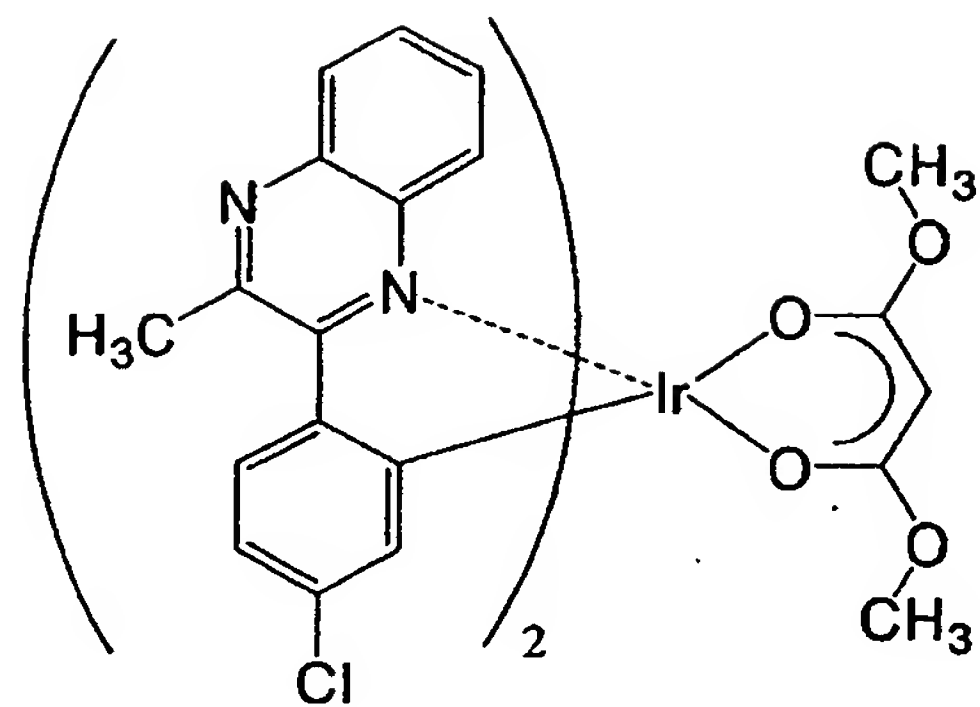
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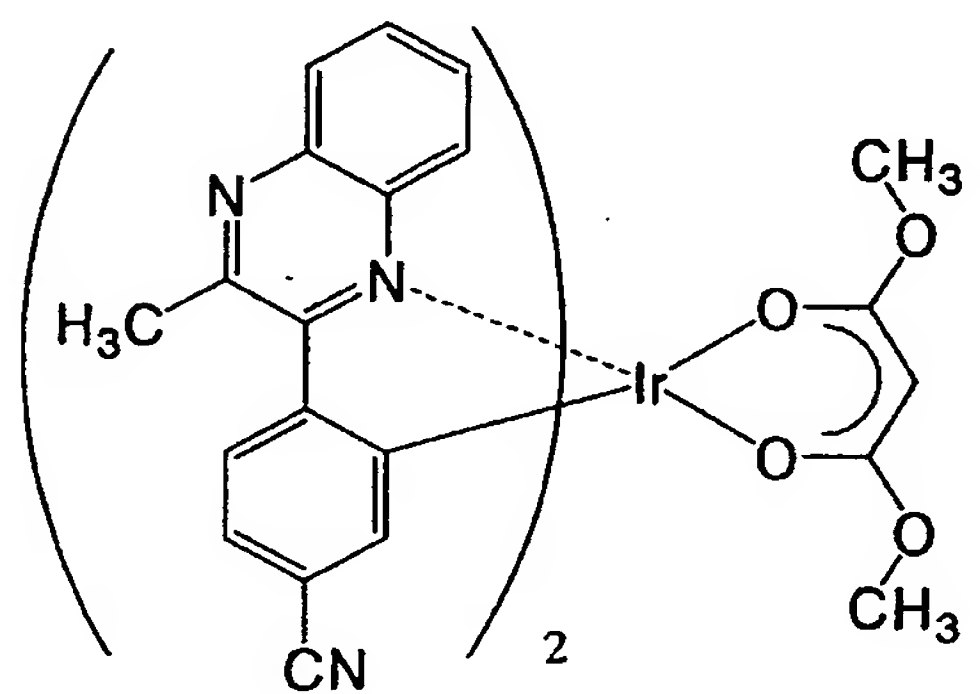
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[0068]



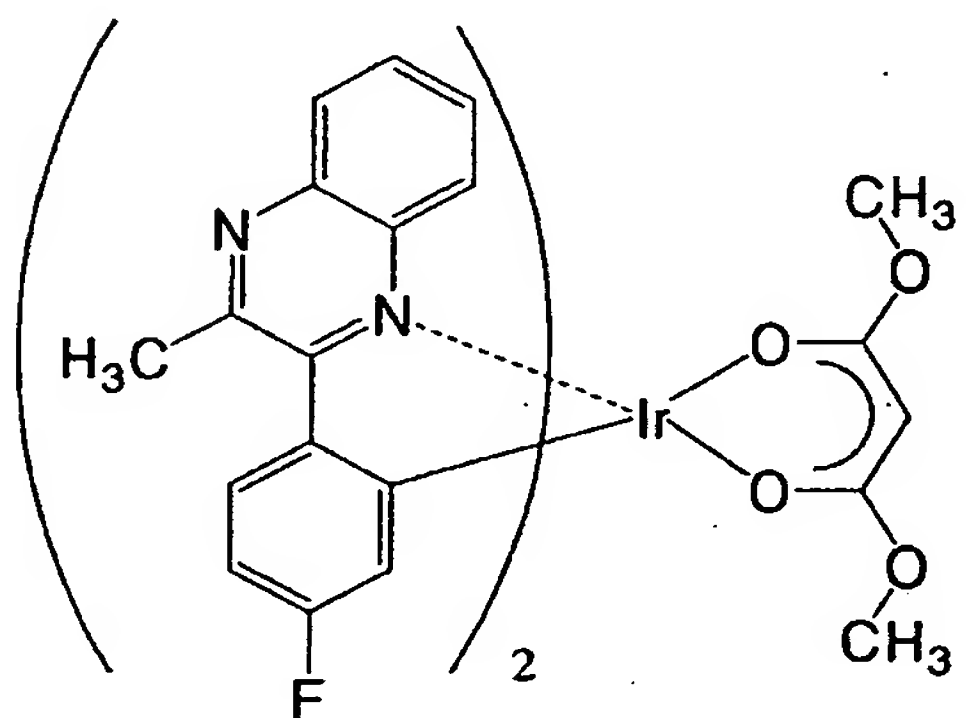
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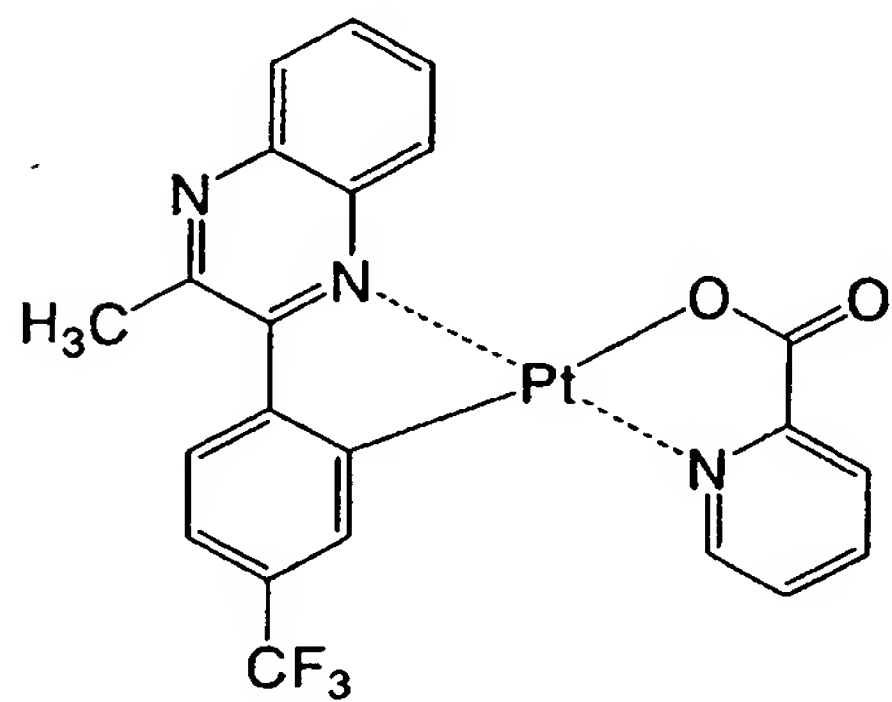
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[0070]



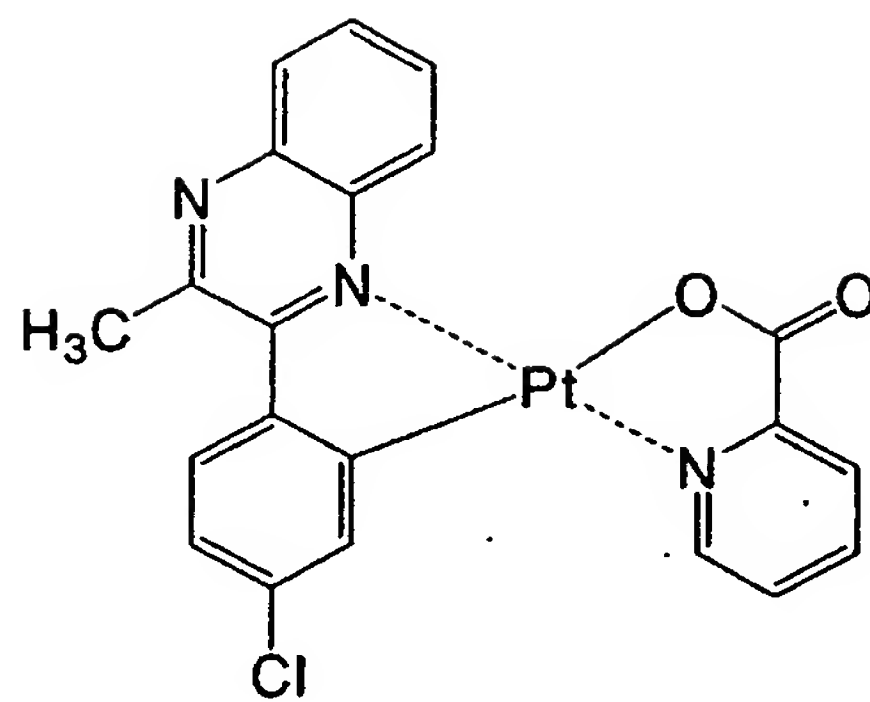
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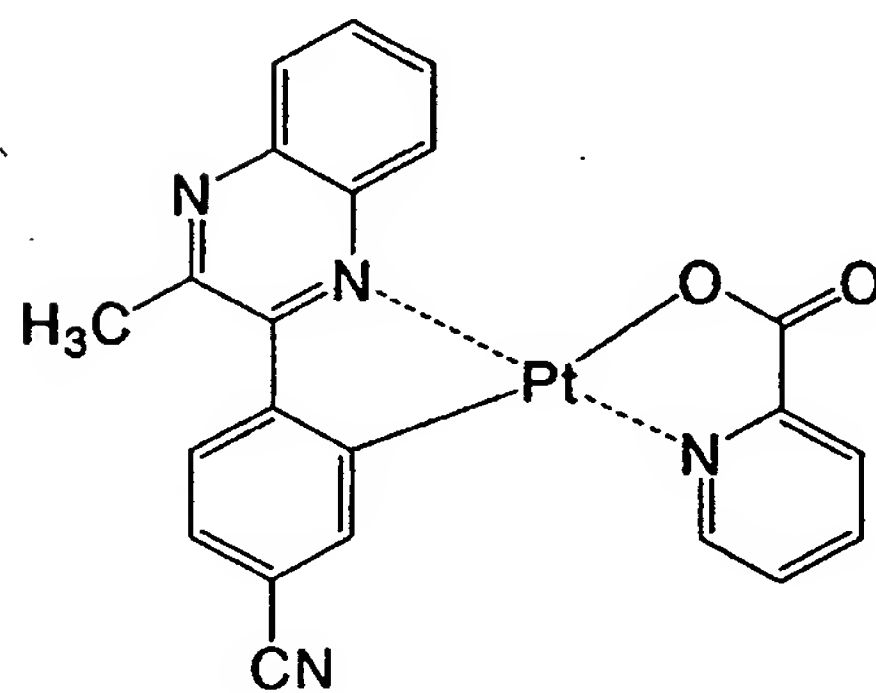
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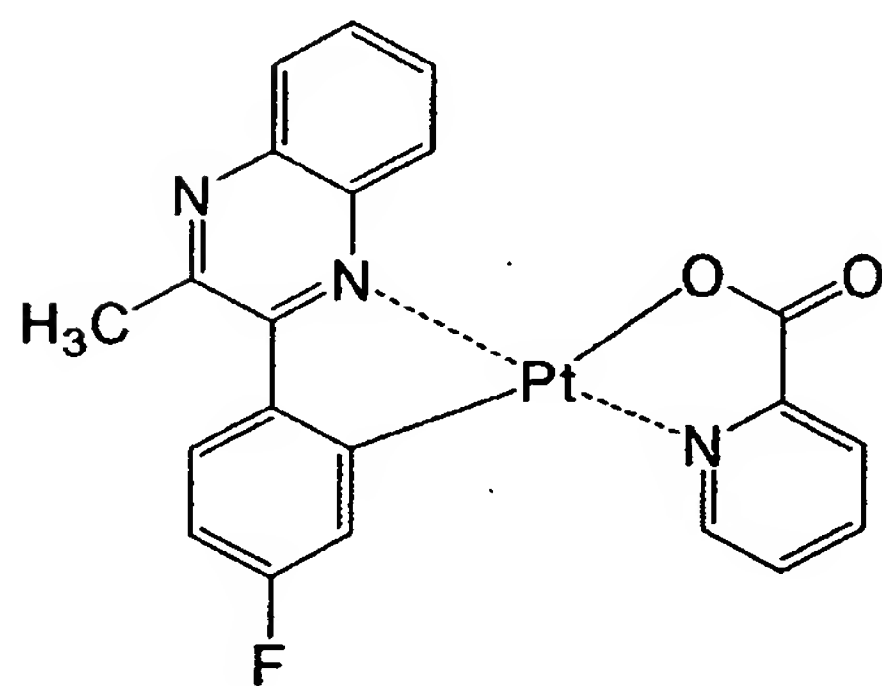
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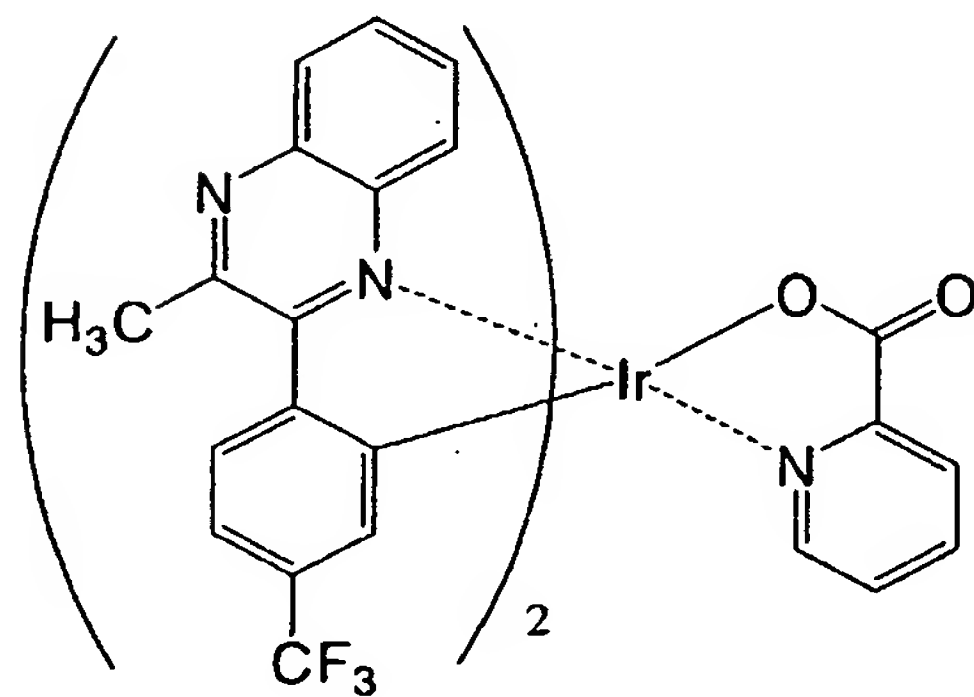
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[0074]



(30)

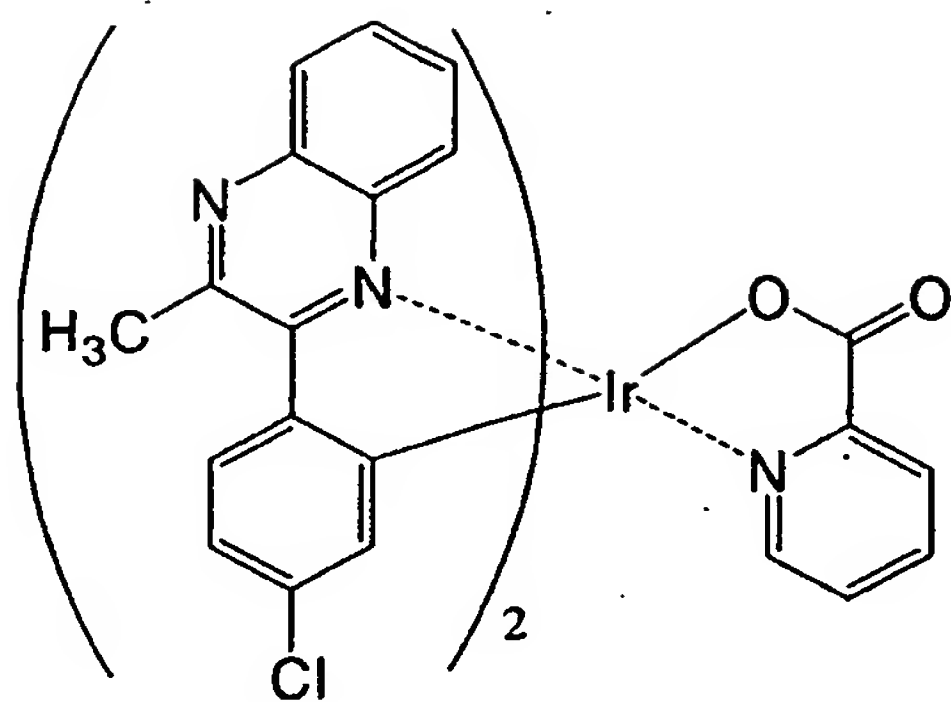
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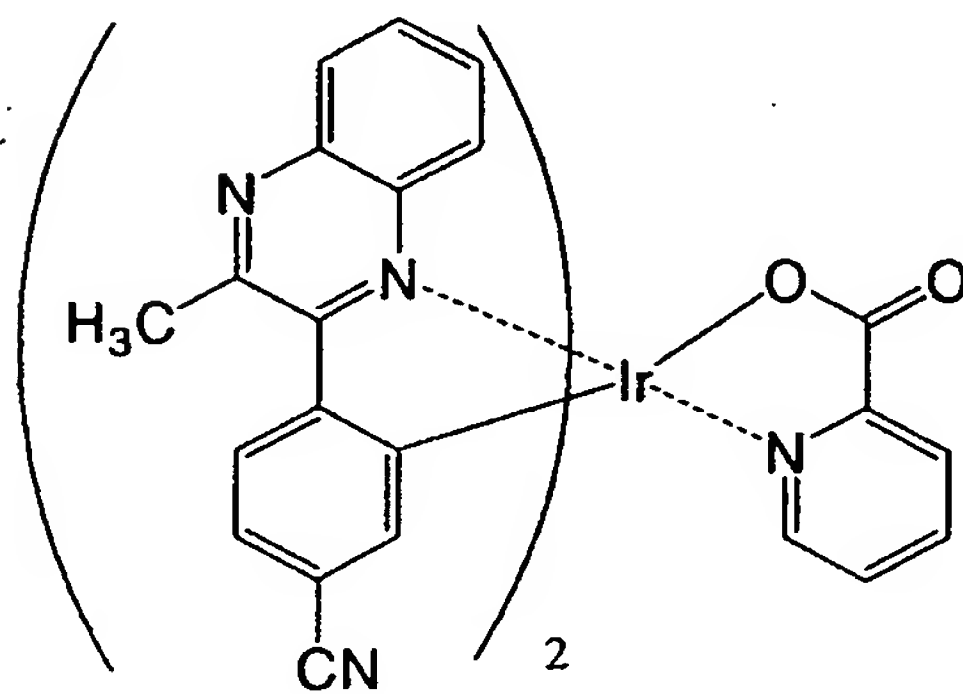
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[0077]

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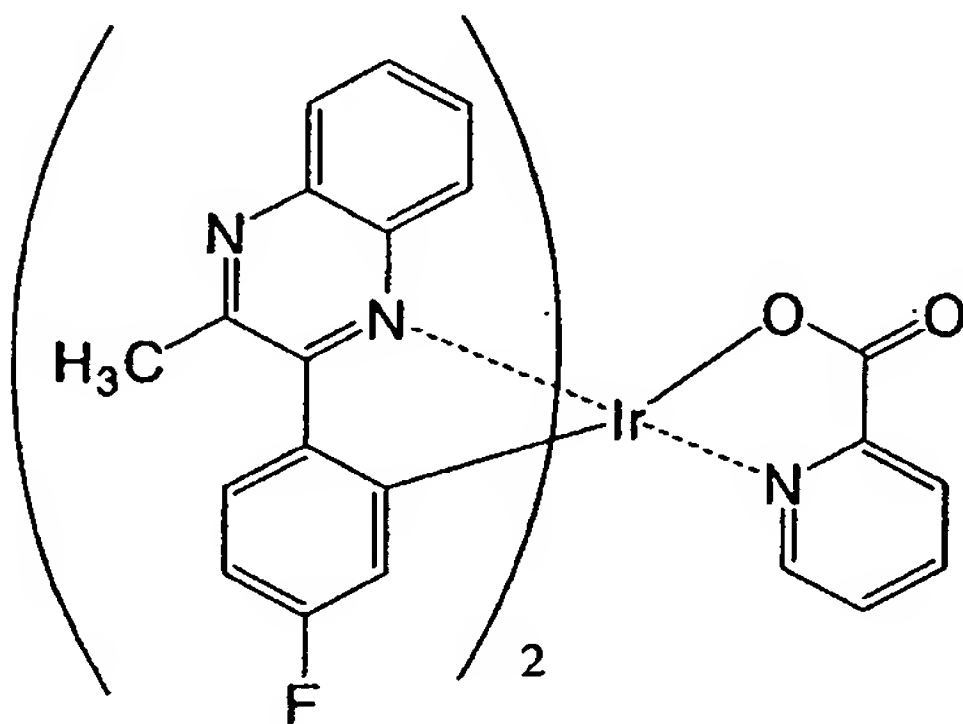


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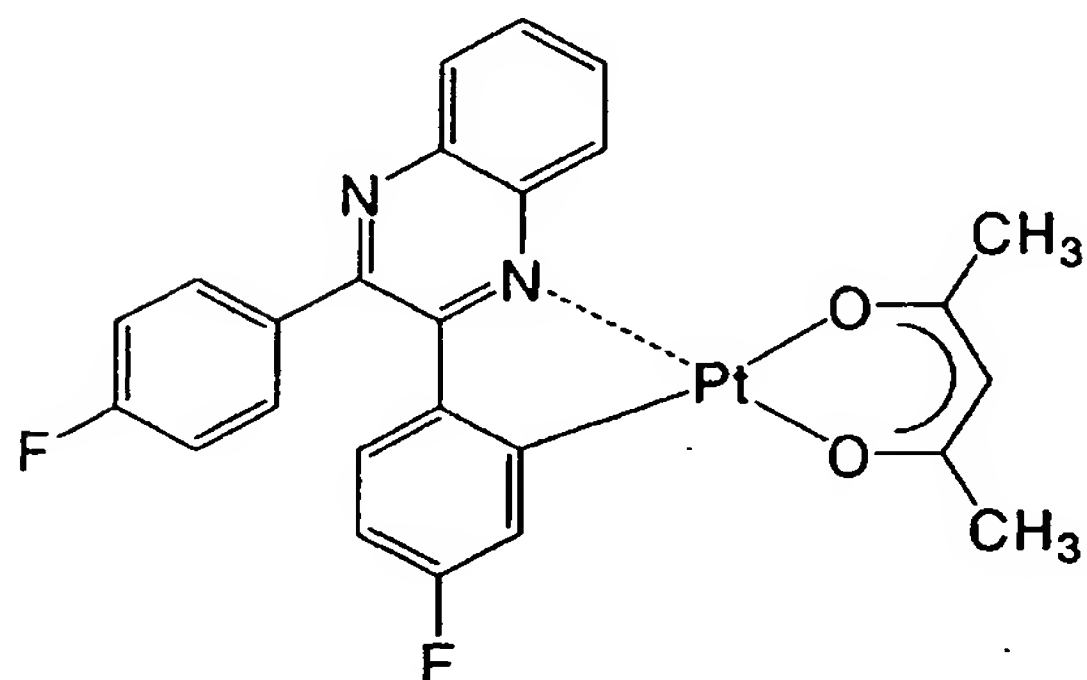
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[0079]

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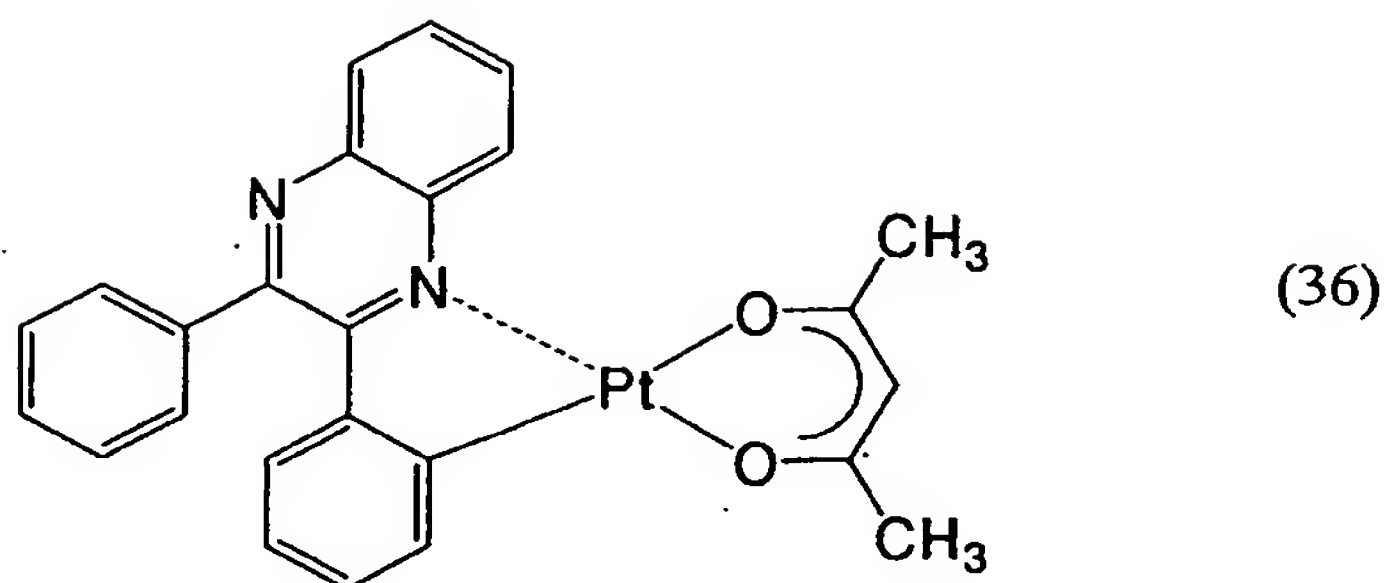


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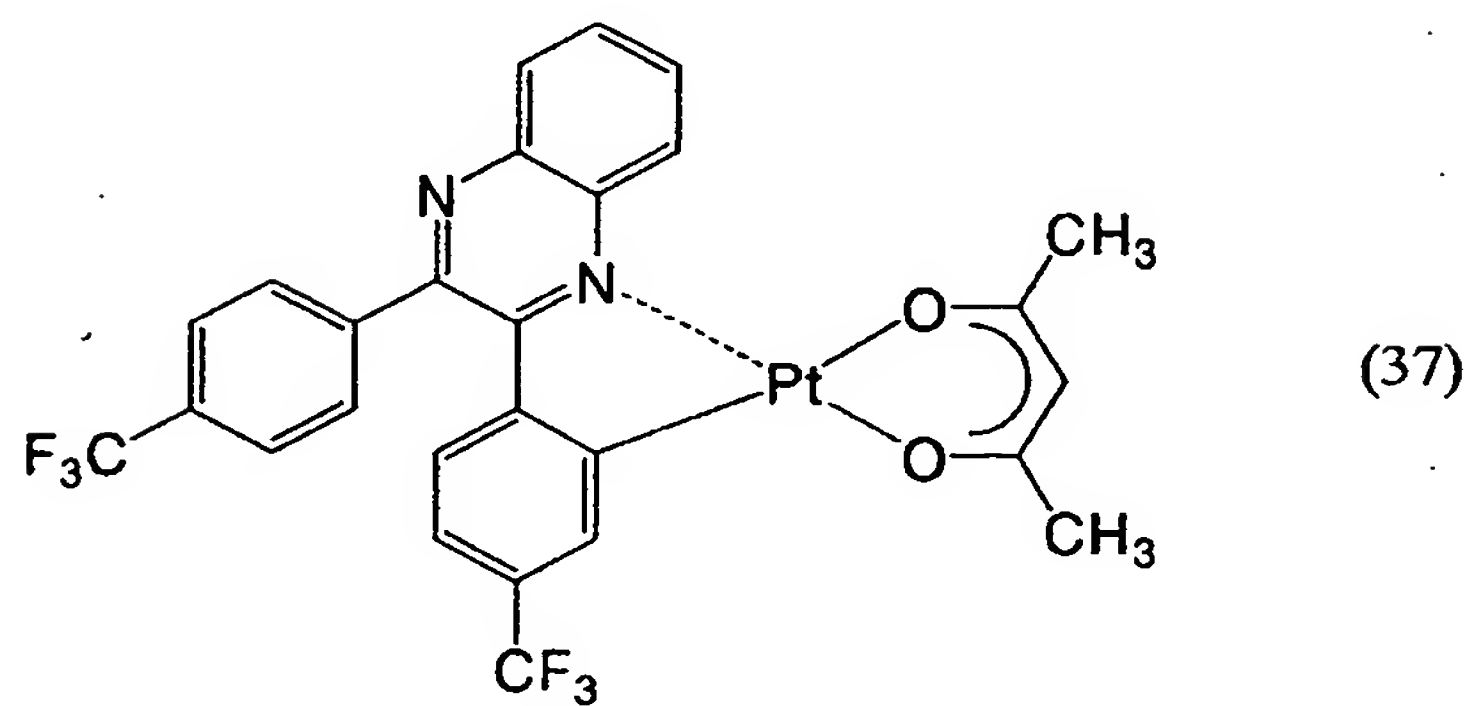
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[0081]

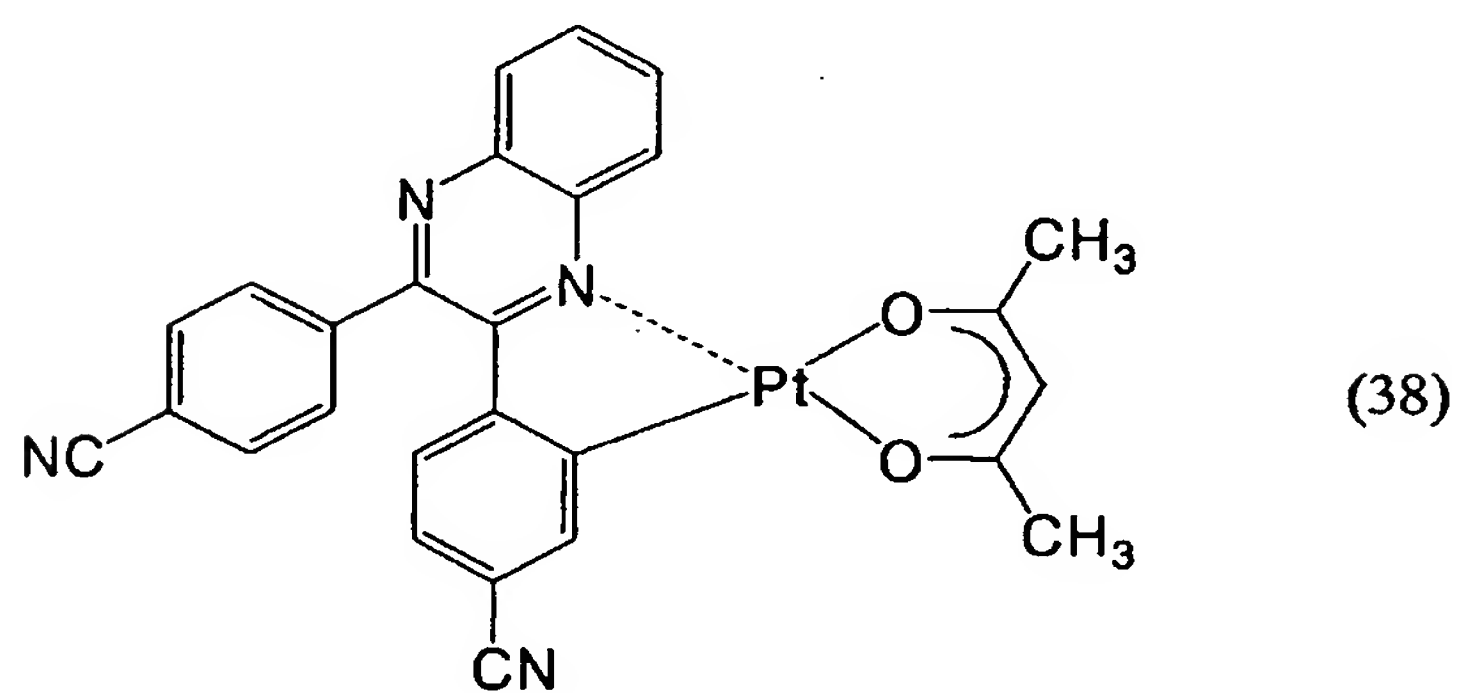
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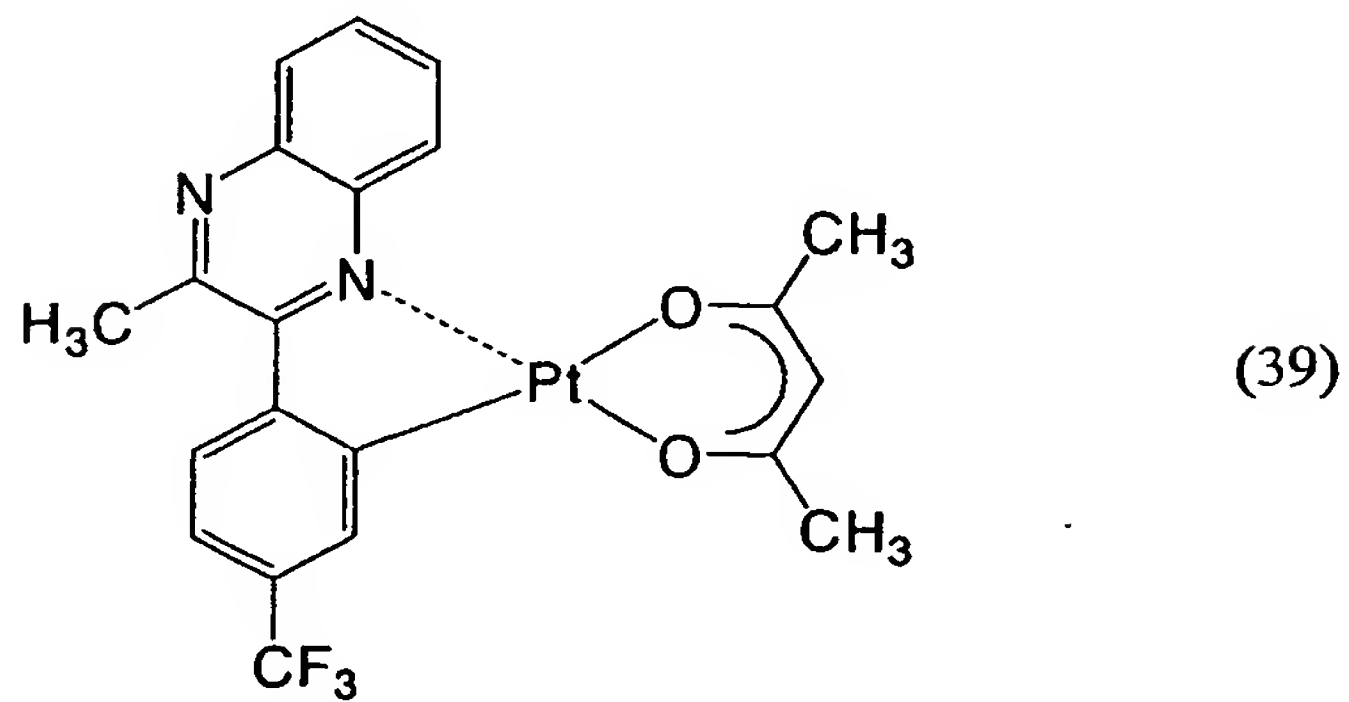
[0082]

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[0083]

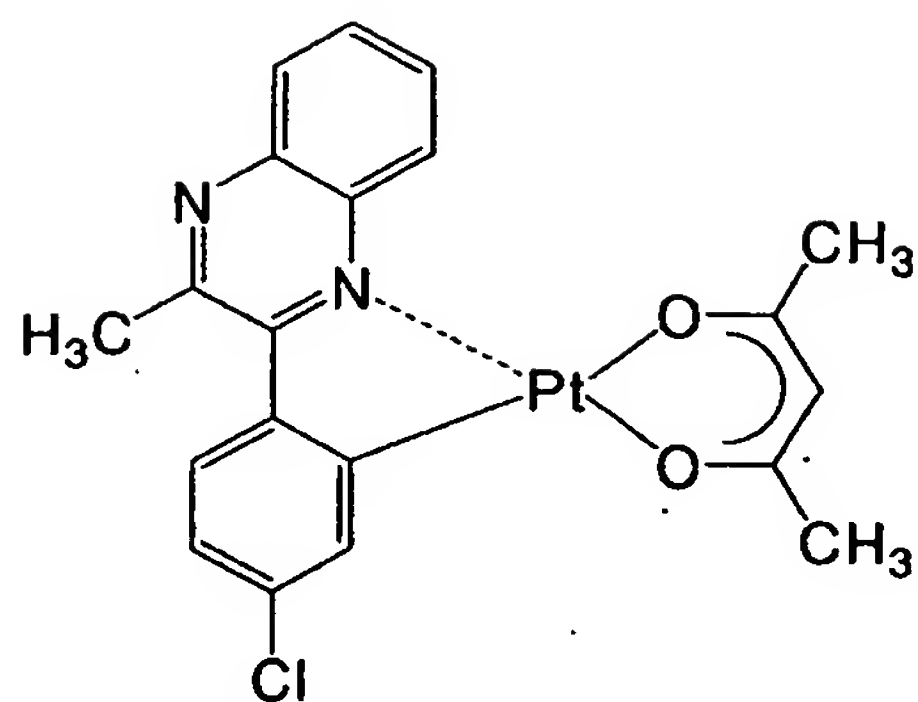
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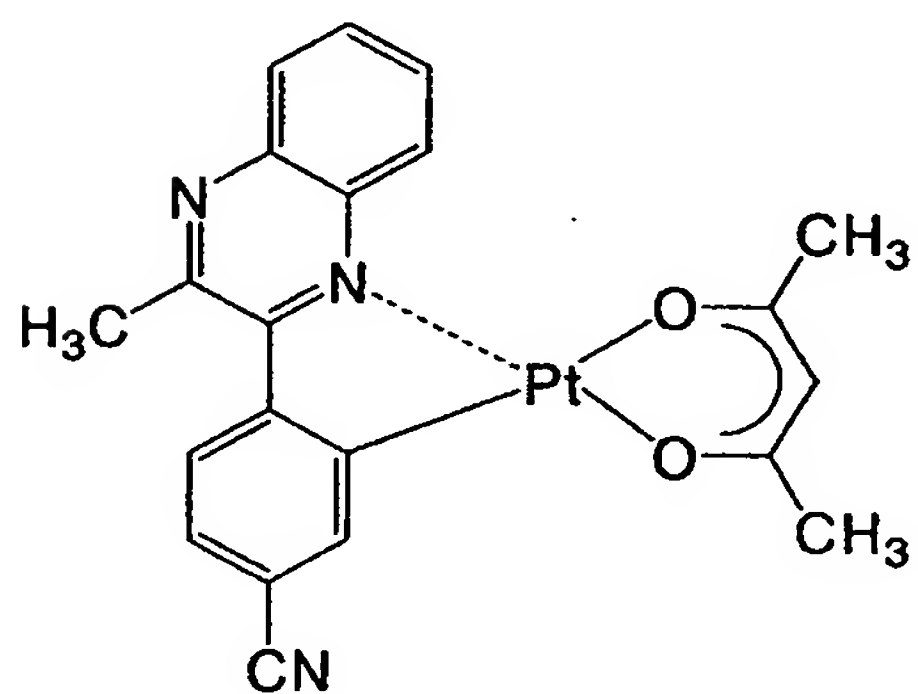
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(40)

[0085]

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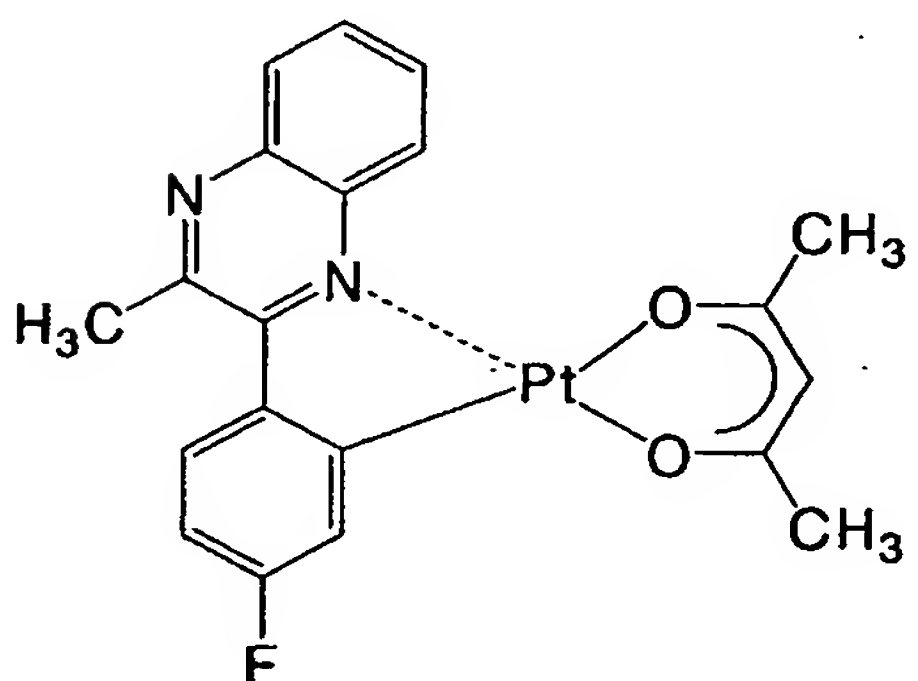


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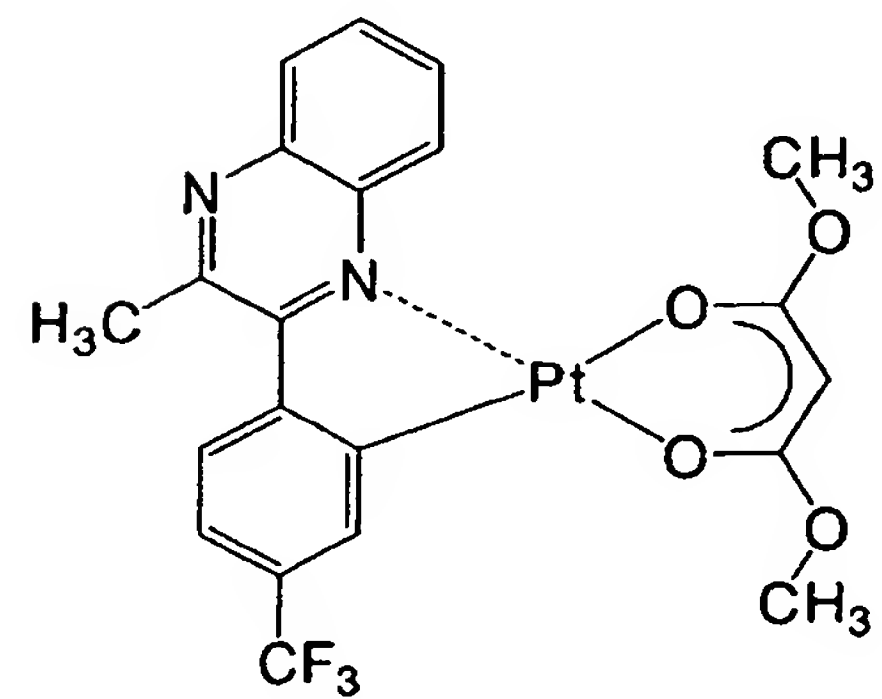
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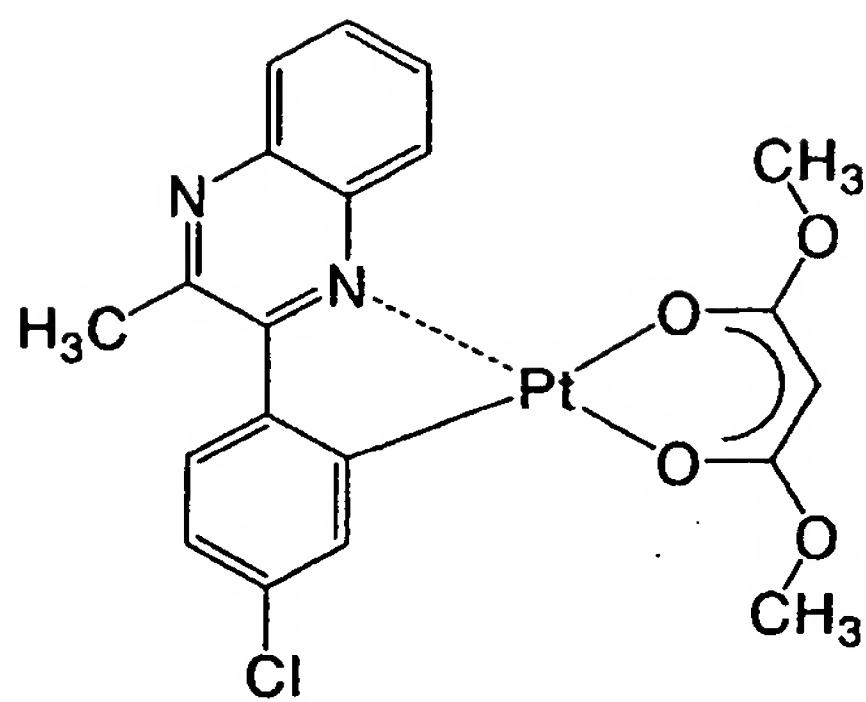
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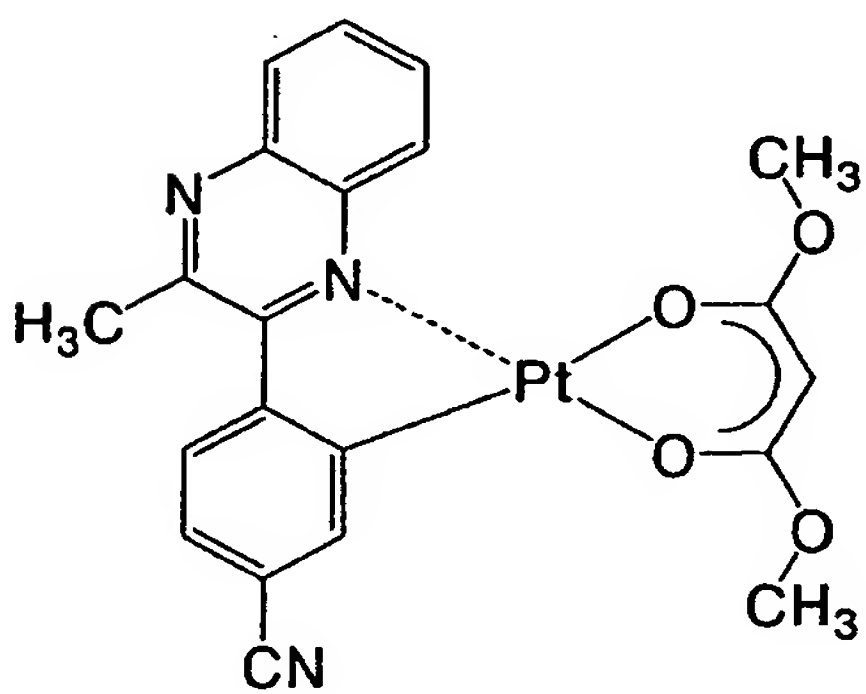
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[0088]



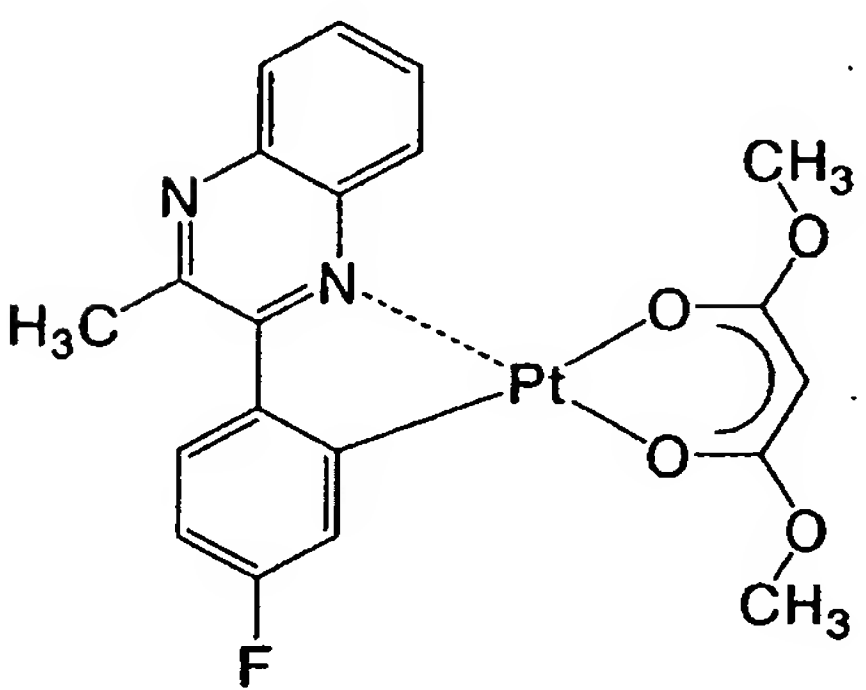
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[0089]



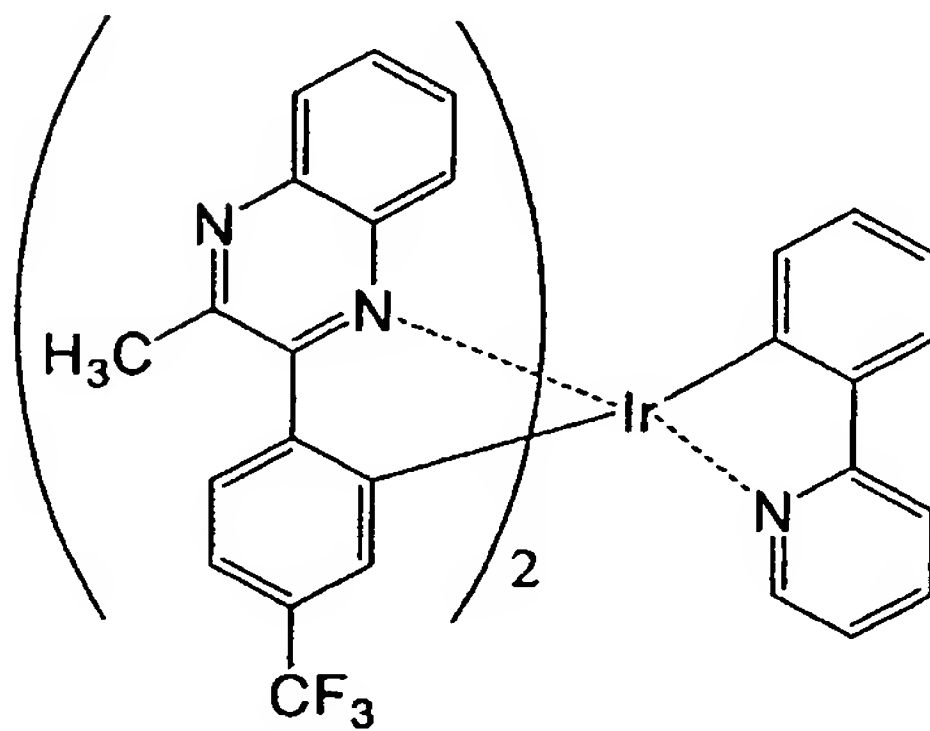
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[0090]



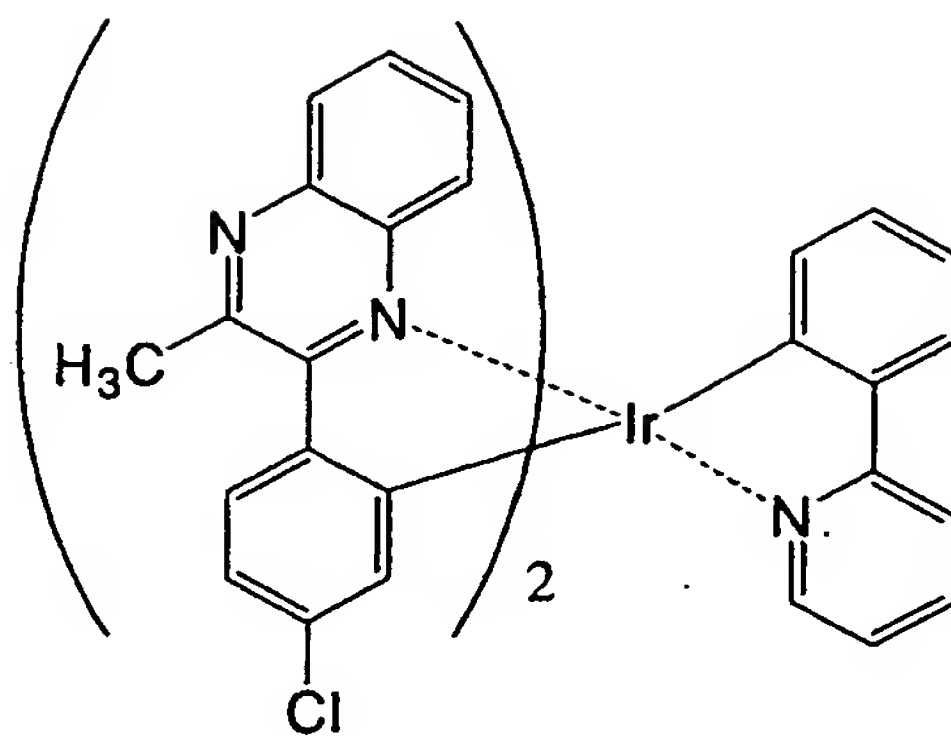
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[0091]



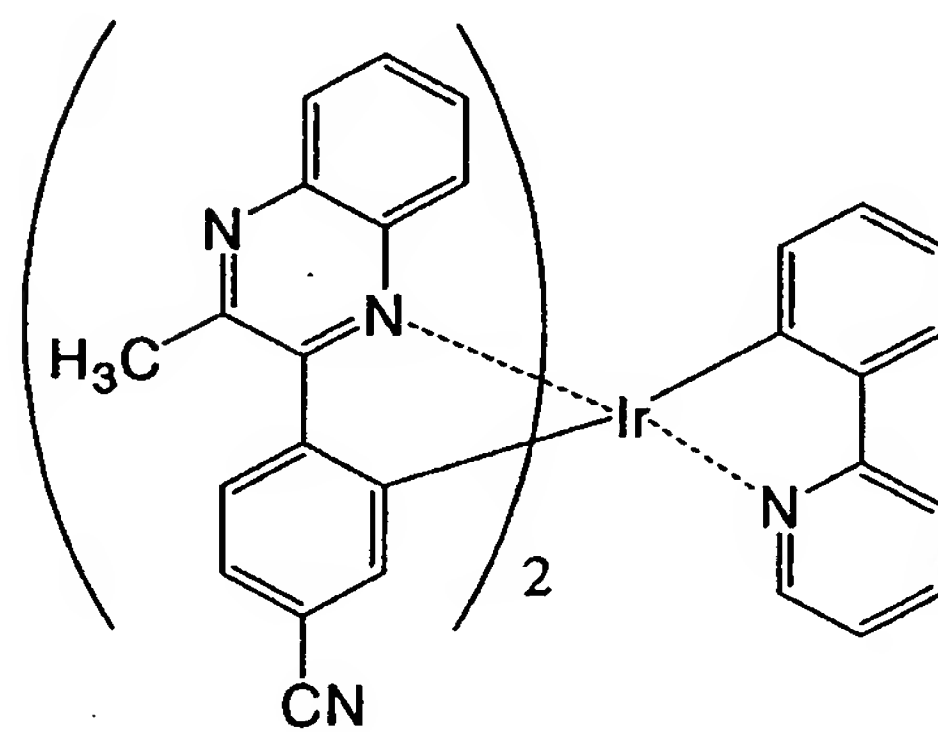
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[0092]



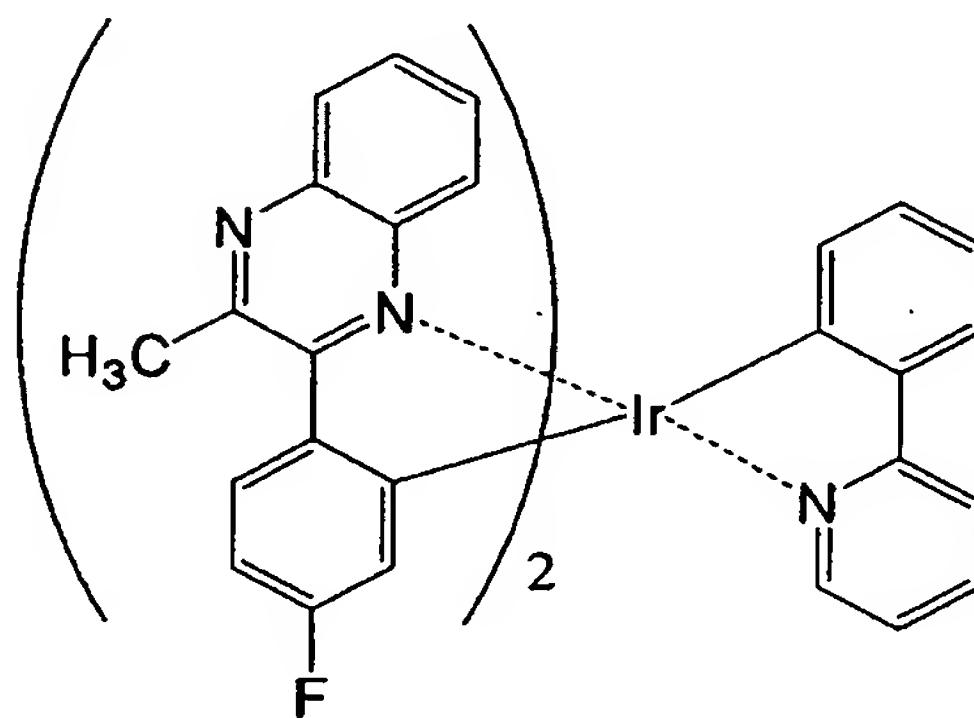
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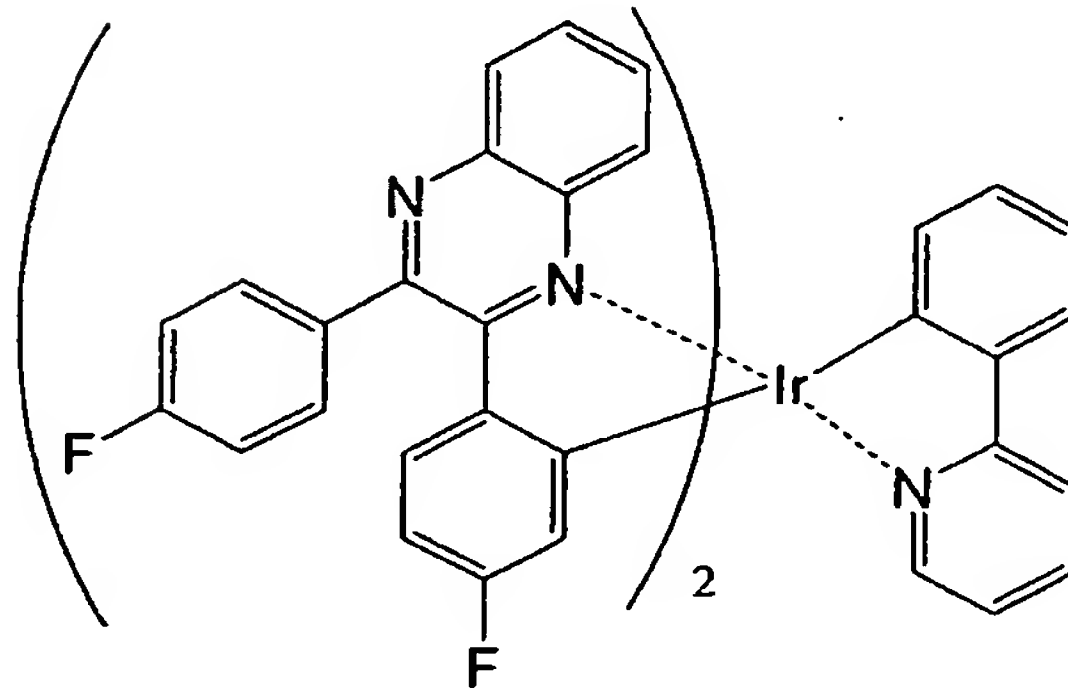
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[0094]



(50)

[0095]

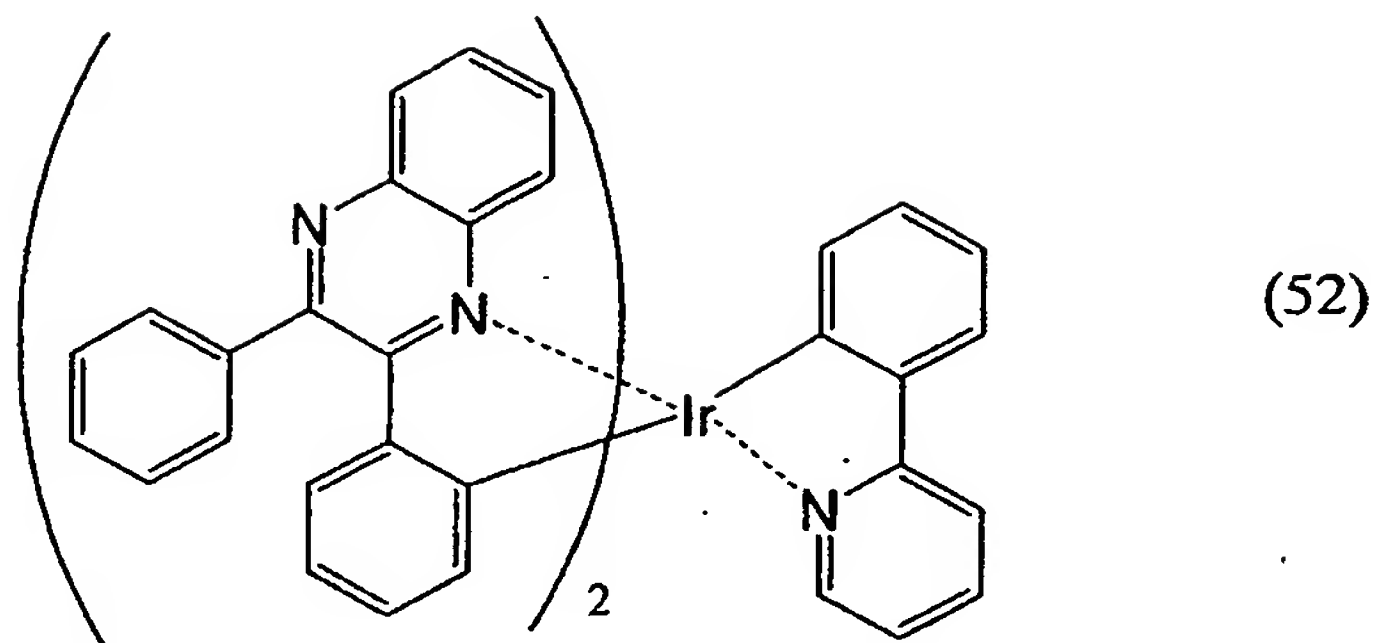


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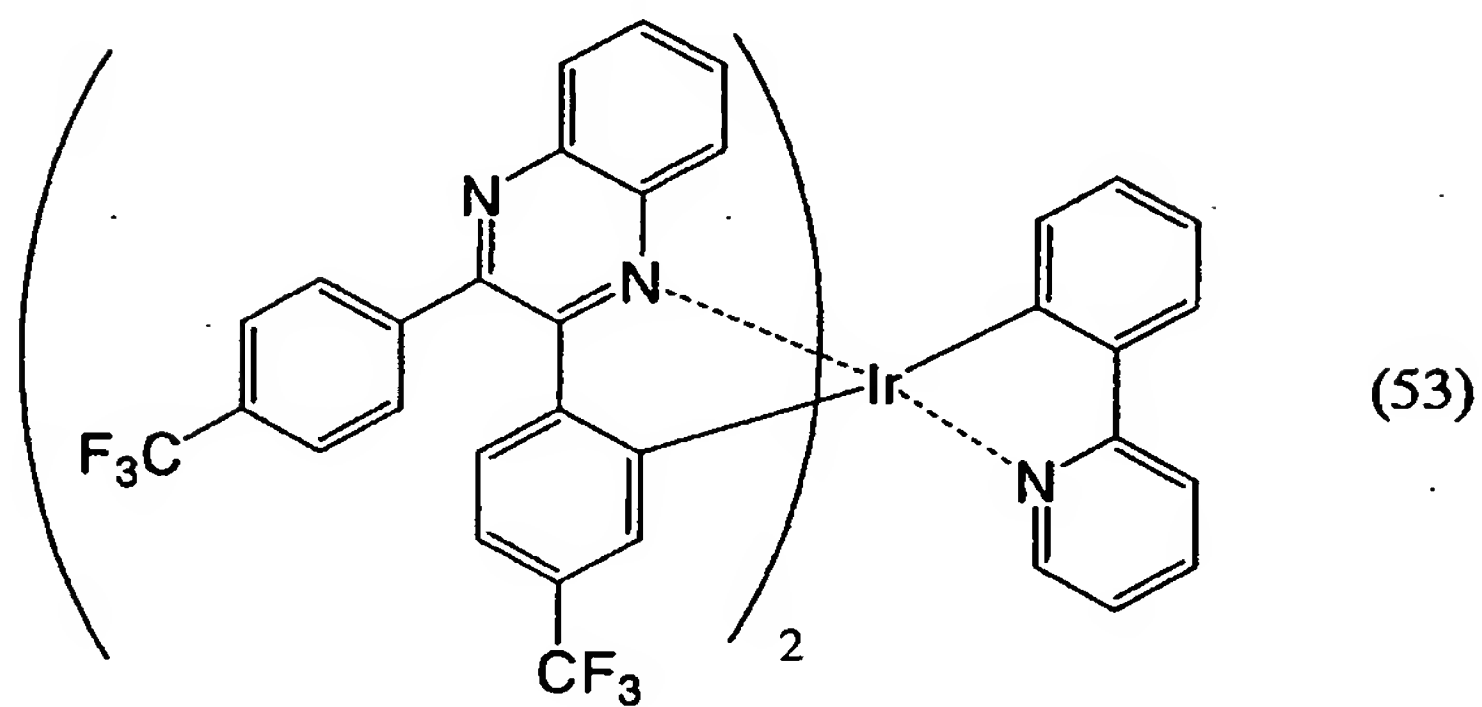
[0096]

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[0097]

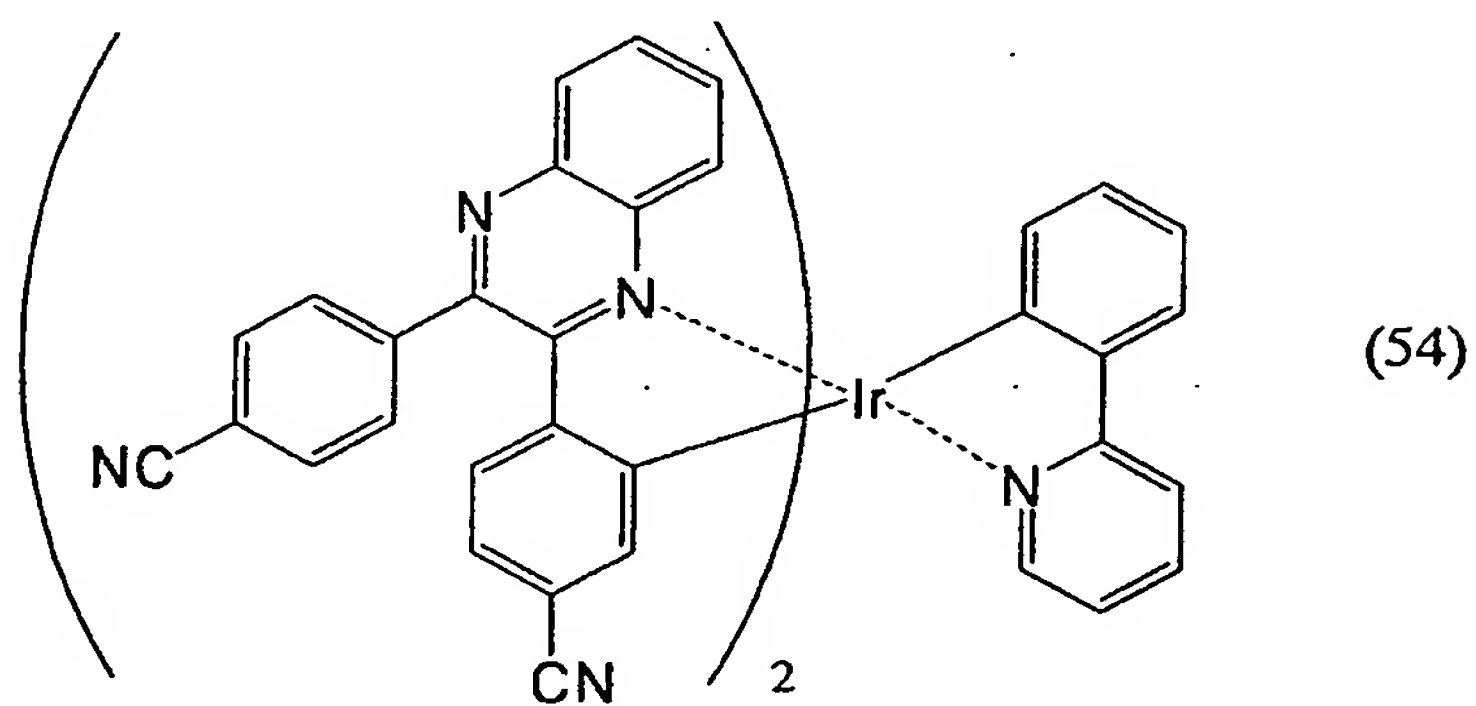
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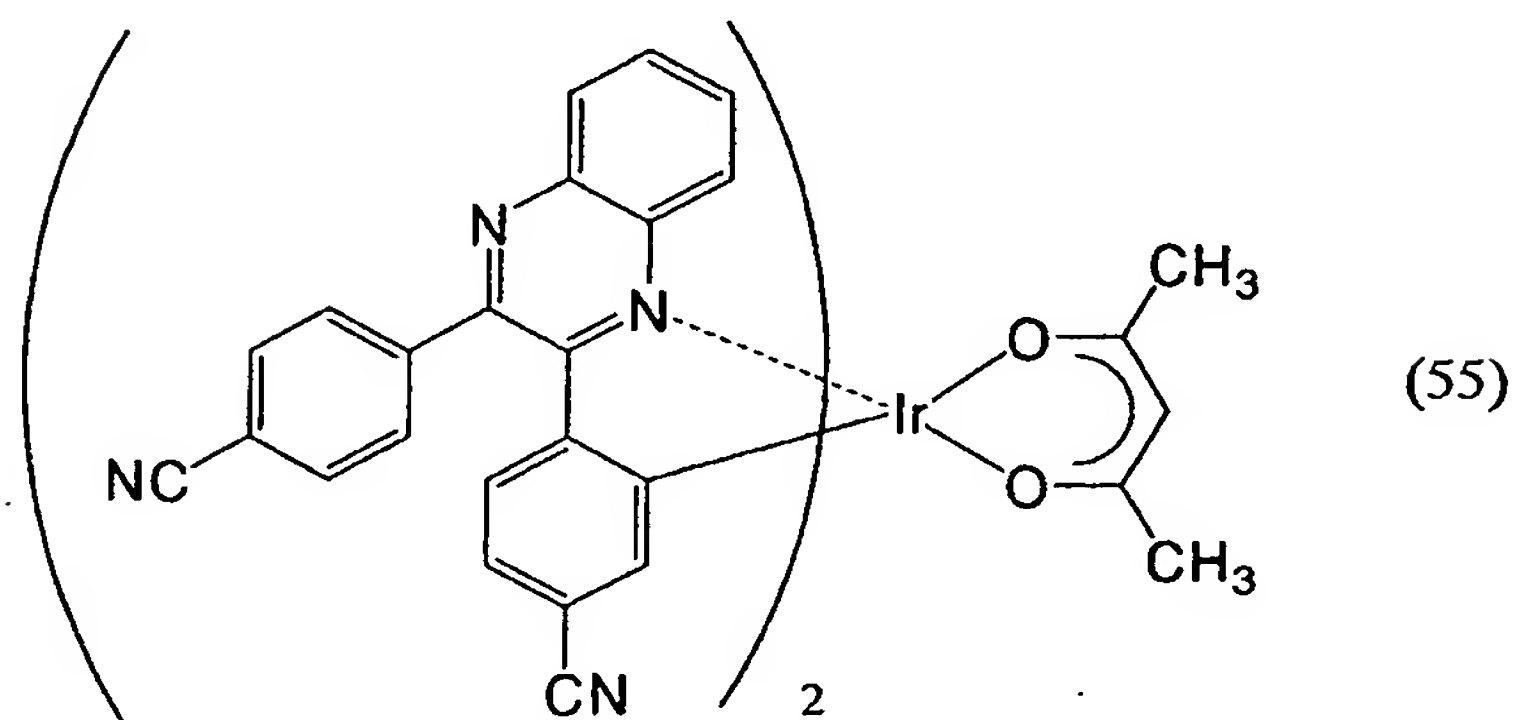
[0098]

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[0099]

25



30

[0100]

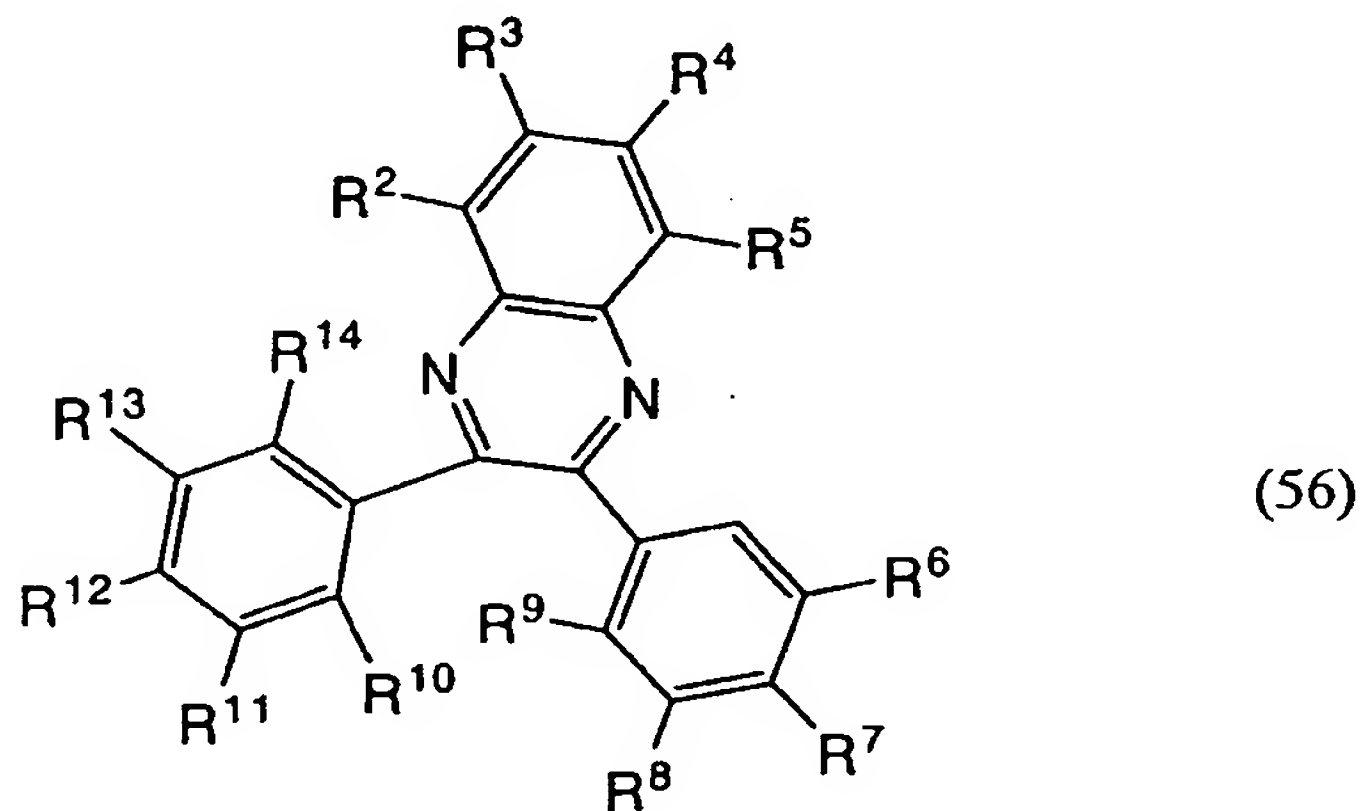
The above-mentioned organometallic complexes according to the present invention are capable of emitting phosphorescence. In addition, the organometallic complexes according to the present invention can be applied to a light-emitting element as a luminescent material. In addition, the organometallic complexes according to the present invention can be applied to a light-emitting element as a photosensitizer.

[0101]

(Synthesis Method of Organometallic Complex according to the Present Invention)

Next, a manufacturing method, that is, a synthesis method of an organometallic complex according to the present invention will be described. An organometallic complex according to the present invention, that is, an organometallic complex including a structure represented by each of the general formulas (1) to (4); that is, an organometallic complex represented by each of the general formulas (5) to (8) can be obtained by orthometallation of a ligand. For example, an organometallic complex including a ligand represented by the following general formula (56), that is, an organometallic complex including a structure represented by the general formula (3) or an organometallic complex represented by the general formula (7), can be obtained by orthometallation of a ligand represented by the following general formula (56). A method for synthesizing an organometallic complex represented by the general formula (7) with the use of a ligand represented by the general formula (56) will be described below.

[0102]



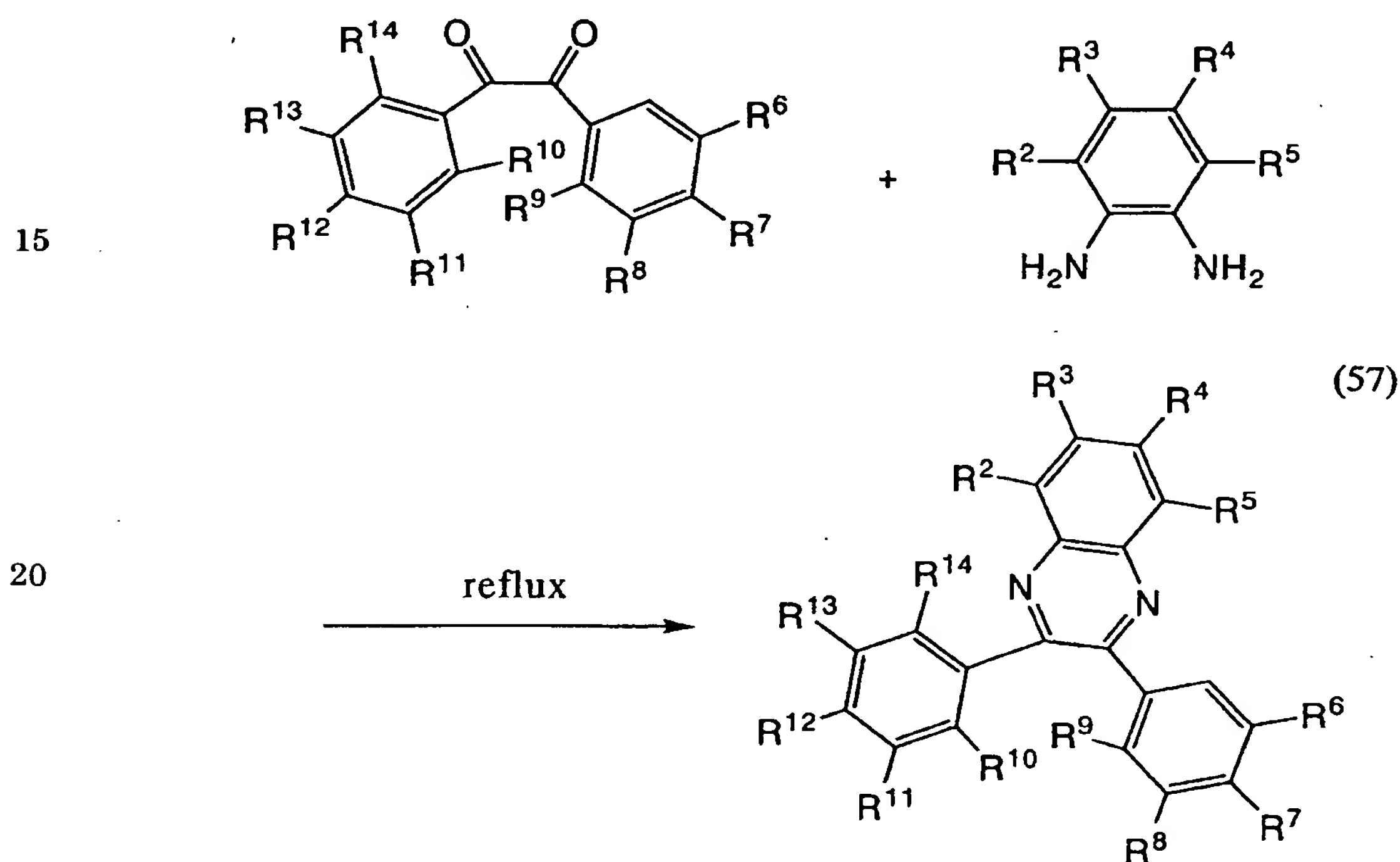
[0103]

In the formula (56), R^2 to R^{14} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group.

[0104]

It is to be noted that a ligand represented by the general formula (56) can be synthesized, for example, in accordance with the following synthesis scheme. In addition, another ligand in an organometallic complex according to the present invention can be synthesized in a similar way.

[0105]



[0106]

In the formula (57), R^2 to R^{14} are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group.

[0107]

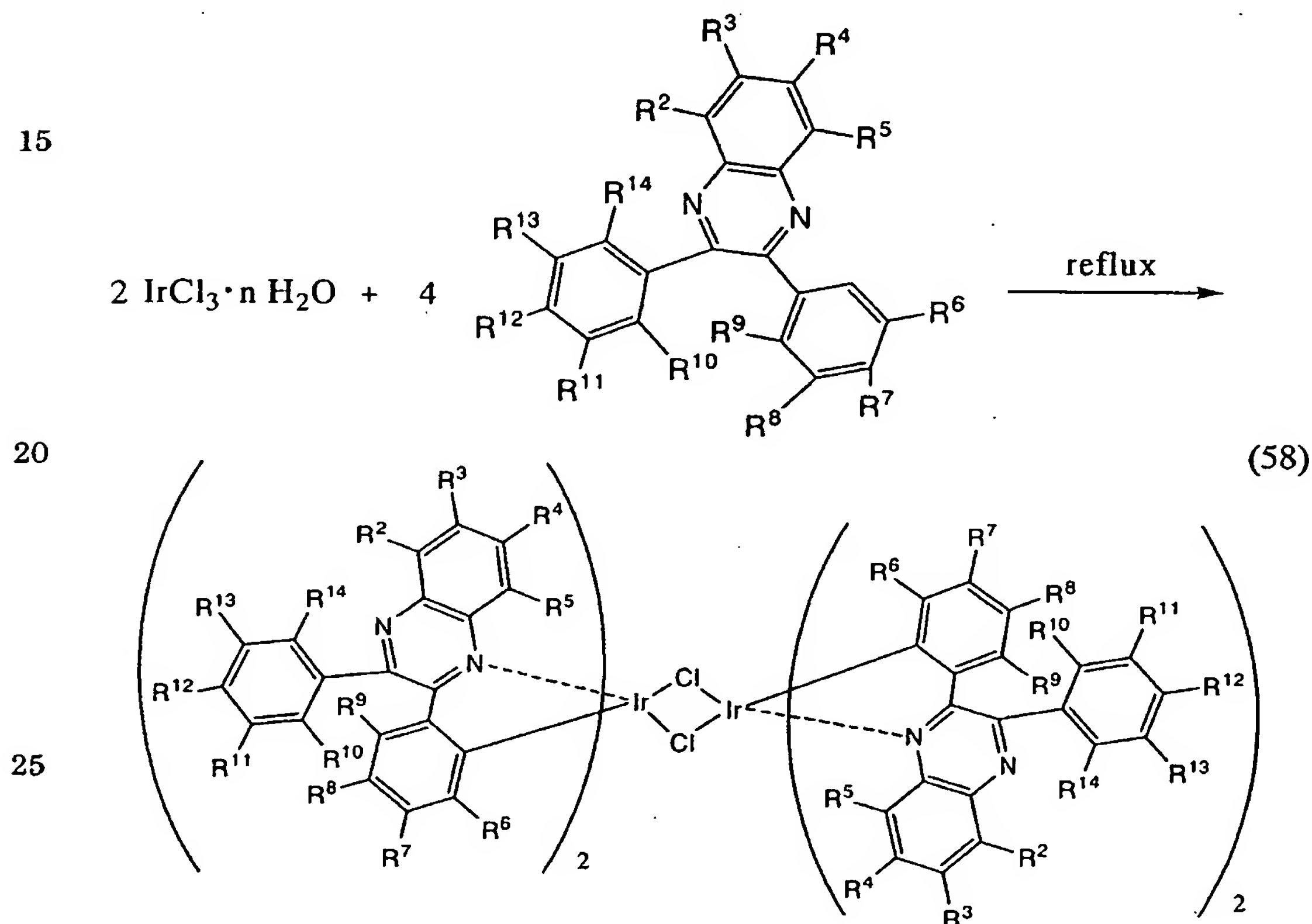
The thus obtained ligand represented by the general formula (56) is used to synthesize an organometallic complex according to the present invention. The following synthesis method may be used for a reaction (orathometallation) in this case.

[0108]

5 For example, when an organometallic complex with iridium as a central metal according to the present invention is synthesized, a chloro-bridged dinuclear complex is first synthesized with the use of iridium chloride hydrate as a raw material for the central metal by mixing the iridium chloride hydrate with the ligand represented by the general formula (56) and holding the iridium chloride hydrate mixed with the ligand at
10 reflux in a nitrogen atmosphere.

[0109]

The synthesis scheme is shown by the following formula (58).



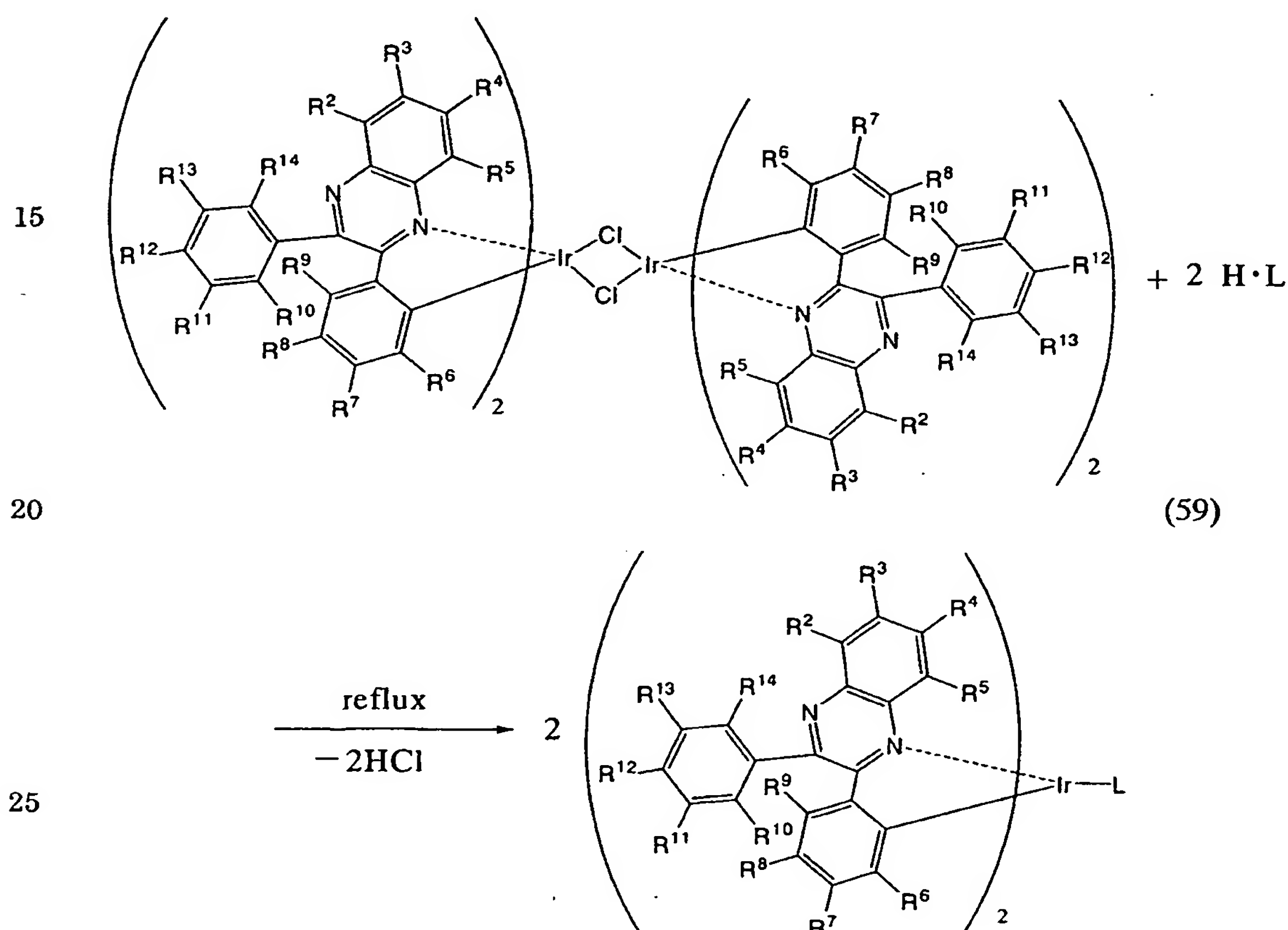
consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group.

[0111]

Next, by mixing the obtained dinuclear complex with a ligand L and holding the dinuclear complex mixed with the ligand L at reflux in a nitrogen atmosphere, the chlorine bridge is cut with the ligand L to obtain an organometallic complex according to the present invention.

[0112]

The synthesis scheme is shown by the following formula (59).



[0113]

In the formula (59), R² to R¹⁴ are individually any one selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl

group, an aryl group, a cyano group, a heterocyclic group, and an electron-withdrawing group.

[0114]

It is to be noted that the synthesis method of an organometallic complex according to the present invention is not to be considered limited to the synthesis method described above.

[0115]

(Embodiment mode modes of Light-Emitting Elements according to the Present Invention)

Next, light-emitting elements according to the present invention will be described with reference to the accompanying drawings.

[0116]

[Embodiment mode 1]

In Embodiment mode 1, a light-emitting element according to the present invention will be described with reference to FIG. 1.

As shown in FIG. 1, the light-emitting element according to the present invention has a structure in which a first electrode 101 is formed on a substrate 100, a layer 102 including a luminescent material is formed on the first electrode 101, and a second electrode 103 is formed thereon. As a material to be used for the substrate 100 here, a material that is used for a conventional light-emitting element may be used. For example, glass, quartz, transparent plastic, and a flexible substrate can be used. In addition, the first electrode 101 and the second electrode 103 in Embodiment mode 1 function as an anode and a cathode, respectively.

[0117]

Namely, the first electrode 101 is formed by using an anode material. As the anode material that can be used here, it is preferable to use a metal, an alloy, an electrically conductive compound, or a mixture thereof, which has a larger work function (a work function of 4.0 eV or more). As specific examples of the anode material, a metal such as gold (Au), platinum (Pt), nickel (Ni), tungsten (W), chromium

(Cr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), or palladium (Pd), and a nitride of a metal material such as TiN can be used in addition to ITO (indium tin oxide), ITSO (indium tin silicon oxide), and IZO (indium zinc oxide) of indium oxide mixed with zinc oxide (ZnO) at 2 to 20 %.

5 [0118]

On the other hand, as a cathode material to be used for the second electrode 103, it is preferable to use a metal, an alloy, an electrically conductive compound, or a mixture thereof, which has a smaller work function (a work function of 3.8 eV or less). As specific examples of the cathode material, in addition to an element belonging to
10 Group 1 or 2 of the periodic table of the elements, that is, alkali metals such as Li and Cs and alkali-earth metals such as Mg, Ca, and Sr, and an alloy (Mg:Ag or Al:Li) and a compound (LiF, CsF, or CaF₂) including the element, a transition metal including a rare-earth metal can be used to form the second electrode 103. The second electrode 103 can be formed also by using a lamination layer of the material mentioned above and
15 a metal (including an alloy) such as Al, Ag, or ITO.

[0119]

A thin film composed of the above-mentioned anode material and a thin film composed of the above-mentioned cathode material are formed by a method such as evaporation or sputtering to form the first electrode 101 and the second electrode 103,
20 respectively, which preferably have a film thickness of 10 to 500 nm. Finally, a protective layer (a barrier layer) composed of an inorganic material such as SiN or an organic material such as Teflon (registered trademark) or a styrene polymer is formed. The barrier layer may be transparent or non-transparent, and the inorganic material or organic material is formed by a method such as evaporation or sputtering.

25 [0120]

In the light-emitting element according to the present invention, light generated by recombination of carriers in a light-emitting layer is emitted from one or both of the first electrode 101 and the second electrode 103 to the outside. Namely, the first electrode 101 is formed by using a light-transmitting material when the light is emitted
30 from the first electrode 101 while the second electrode 103 is formed by using a

light-transmitting material when the light is emitted from the second electrode 103. The layer 102 including the luminescent material is formed by stacking a plurality of layers, in Embodiment mode 1, by stacking a hole injecting layer 111, a hole transporting layer 112, a light-emitting layer 113, a hole blocking layer 114, and an
5 electron transporting layer 115 in order.

[0121]

In the layer 102 including the luminescent material, the hole injecting layer 111 is provided to come in contact with the first electrode 101. In addition, it is preferable to form the hole injecting layer 111 with the use of a material that is capable of
10 receiving holes from the first electrode 101, and further, be formed with a material that is capable of injecting holes into a layer provided on the second electrode 103 side of the hole injecting layer 111 to come in contact with the hole injecting layer 111. Specifically, it is preferable to form the hole injecting layer 111 with the use of a phthalocyanine compound. The phthalocyanine compound includes, for example,
15 phthalocyanine (abbreviation: H₂-Pc) and copper phthalocyanine (abbreviation: Cu-Pc).

[0122]

In addition, aromatic amine compounds such as 4, 4' - bis [N - {4 - (N, N - di - m - tolylamino) phenyl} - N - phenylamino] biphenyl (abbreviation: DNTPD) and 4, 4', 4'' - tris [N - (3 - methylphenyl) - N - phenylamino] - triphenylamine (abbreviation:
20 MTDATA). In addition, conductive inorganic compounds (including semiconductors) such as molybdenum oxide (MoOx) and vanadium oxide (VOx) can be also used. Further, a mixture of the conductive inorganic compound and the aromatic amine compound described above or below can be used. This mixture can be formed by a method such as co-evaporation.

25 [0123]

It is preferable to form the hole transporting layer 112 with the use of a material that is capable of transporting holes, specifically, an aromatic amine compound (that is, a compound having a benzene ring-nitrogen bond). For example, in addition to 4, 4' - bis [N - (3 - methylphenyl) - N - phenyl - amino] - biphenyl (abbreviation:
30 TPD) and 4, 4' - bis [N - (1 - naphthyl) - N - phenyl - amino] - biphenyl (abbreviation:

α -NPD), starburst aromatic amine compounds such as MTDATA mentioned above and 4, 4', 4'' - tris (N, N - diphenyl - amino) - triphenylamine (abbreviation: TDATA) are preferably used to form the hole transporting layer 112. In addition, a mixture of a conductive inorganic compound (including semiconductors) such as molybdenum oxide (MoOx) or vanadium oxide (VOx) and the aromatic amine compound described above
5 can be used. This mixture can be formed by a method such as co-evaporation.

[0124]

It is preferable that the light-emitting layer 113 be formed by co-evaporation of at least one organometallic complex and a host material. The organometallic complex
10 is an organometallic complex including a structure represented by one of the general formulas (1) to (4), or an organometallic complex represented by one of the general formulas (5) to (8). As the host material, it is preferable to use a material that has a larger energy gap (E_g) than the organometallic complex, which has a structure represented by one of the general formulas (1) to (4), or is represented by one of the
15 general formulas (5) to (8).

[0125]

In addition, in particular, as the host material, it is preferable to use a material that has a larger energy gap and further has a larger ionization potential (I_p) and a smaller electron affinity (EA) than the organometallic complex, which has a structure
20 represented by one of the general formulas (1) to (4), or is represented by one of the general formulas (5) to (8). Examples thereof include 4, 4' - bis (N - carbazoyl) - biphenyl (abbreviation: CBP), 4, 4', 4'' - tris (N - carbazoyl) - triphenylamine (abbreviation: TCTA), and 1, 3, 5 - tris [4 - (N - carbazoyl) phenyl] benzene (abbreviation: TCPB). Further, it is more preferable that the host material be
25 composed of a material that is capable of transporting either one or both carriers of a hole and an electron, specifically, a material that has a carrier mobility of 10^{-6} cm²/Vs or more. This makes it possible to reduce the driving voltage and improve the reliability of the element.

[0126]

30 Specific examples of materials that can be used as the host material include

α -NPD and tris (8 - quinolinolato) aluminum (abbreviation: Alq₃). It is to be noted that the hole mobility in α -NPD is approximately 10^{-4} cm²/Vs, and that the electron mobility in tris (8 - quinolinolato) aluminum (abbreviation: Alq₃) is approximately 10^{-5} cm²/Vs. As described above, it is preferable that the mobilities of either one or both carriers of a hole and an electron be 10^{-6} cm²/Vs or more. However, the host material is not to be considered limited to α -NPD and Alq₃, and the above-mentioned aromatic amine compounds such as TPD and metal complexes such as tris (8 - quinolinolato) gallium (abbreviation: Gaq₃) and tris (4 - methyl - 8 - quinolinolato) aluminum (abbreviation: Almq₃) can be also used as the host material. These materials, Alq₃, Gaq₃, and Almq₃, correspond to examples of electron transporting metal complexes.

[0127]

When the light-emitting layer 113 is formed to have the structure described above, holes and electrons are easily transported in the light-emitting layer 113, and those holes and electrons are efficiently trapped in the organometallic complex without passing through the light-emitting layer to produce luminescence. Therefore, it is not easy for holes or electrons to pass through the light-emitting layer, and exciton formation is made more efficient. Accordingly, a stable device that shows less decrease in luminous efficiency (that is, deterioration in luminance) can be constructed.

[0128]

The organometallic complexes represented by the formulas (16) to (55) easily receive holes due to the organic moiety-metal bond, and further, easily receive also electrons due to the quinoxaline skeleton. Therefore, the organometallic complexes have the advantage that carriers can be trapped effectively.

[0129]

It is to be noted that it is preferable to form the light-emitting layer 113 with the use of an organometallic complex having a fluoro group or a trifluoromethyl group, particularly, such as the organometallic complexes represented by the formulas (16) and (18) among the organometallic complexes represented by the formulas (16) to (55). This expands the range of choices for the host materials. In addition, in particular, the affinity for electrons is increased to provide the advantage that electrons can be trapped

more effectively.

[0130]

It is preferable to form the hole blocking layer 114 with the use of a material that has a large ionization potential such as bis (2 - methyl - 8 - quinolinolato) - 4 - phenylphenolato - aluminum (abbreviation: BALq), 1, 3 - bis [5 - (p - tert - butylphenyl) - 1, 3, 4 - oxadiazole - 2 - yl] benzene (abbreviation: OXD-7), 3 - (4 - tert - butylphenyl) - 4 - phenyl - 5 - (4 - biphenyl) - 1, 2, 4 - triazole (abbreviation: TAZ), 3 - (4 - tert - butylphenyl) - 4 - (4 - ethylphenyl) - 5 - (4 - biphenyl) - 1, 2, 4 - triazole (abbreviation: p-EtTAZ), bathophenanthroline (abbreviation: BPhen), or bathocuproin (abbreviation: BCP), and more preferable to form the hole blocking layer 114 with the use of a material that has an at least 0.3 eV larger ionization potential than the light-emitting layer 113. This makes it possible to prevent holes injected from the first electrode 101 side into the layer 102 including the luminescent material from flowing toward the second electrode 103 to serve as a cathode. In addition, light energy can be prevented from transferring toward the electron transporting layer 115.

[0131]

It is preferable to form the electron transporting layer 115 with the use of a material that is capable of transporting, toward the light-emitting layer 113, electrons injected from the second electrode 103 to serve as a cathode into the layer 102 including the luminescent material. In addition, it is preferable to form the electron transporting layer 115 with the use of a material that has a larger ionization potential than the material forming the light-emitting layer 113. However, in the case of providing a hole blocking layer 114 as in the present embodiment mode, it is not always necessary to use a material that has a larger ionization potential than the material forming the light-emitting layer 113.

[0132]

Specific examples of such a material include metal complexes having a quinoline skeleton or a benzoquinoline skeleton such as Alq₃, Gaq₃, Almq₃, and bis (10 - hydroxybenzo [h] - quinolinato) beryllium (abbreviation: BeBq₂), and BALq mentioned above. In addition, metal complexes having an oxazole ligand or a thiazole ligand

such as bis [2 - (2 - hydroxyphenyl) - benzoxazolato] zinc (abbreviation: Zn(BOX)₂) and bis [2 - (2 - hydroxyphenyl) - benzothiazolato] zinc (abbreviation: Zn(BTZ)₂) can be also used as a material for forming the electron transporting layer 115. Further, in addition to 2 - (4 - biphenyl) - 5 - (4 - tert - butylphenyl) - 1, 3, 4 - oxadiazole (abbreviation: PBD), and OXD-7, TAZ, p-EtTAZ, BPhen, and BCP mentioned above,
5 inorganic materials such as titanium oxide may be also used.

[0133]

The above-described light-emitting element according to the present invention shows less decrease in luminance over emission time, and shows a favorable lifetime.

10

[0134]

[Embodiment mode 2]

A light-emitting element according to the present invention will be described with reference to FIG. 2.

15 The light-emitting element shown in FIG. 2 has a first electrode 201 on a substrate 200 to serve as a cathode, a layer 202 including a luminescent material on the first electrode, and a second electrode 203 on the layer 202 including the luminescent material to serve as an anode. As shown in FIG. 2, the layer 202 including the luminescent material is formed by stacking an electron transporting layer 211, a hole
20 blocking layer 212, a light-emitting layer 213, a hole transporting layer 214, and a hole injecting layer 215 in order, where the electron transporting layer 211 and the hole transporting layer 214 are provided respectively on the first electrode 201 side and on the second electrode 203 side with the light-emitting layer 213 as a center.

[0135]

25 The electron transporting layer 211, the hole blocking layer 212, the light-emitting layer 213, the hole transporting layer 214, and the hole injecting layer 215 may be formed by evaporation or the like respectively with the use of the same materials as those for the electron transporting layer 115, the hole blocking layer 114, the light-emitting layer 113, the hole transporting layer 112, and the hole injecting layer
30 111 described in Embodiment mode 1. As described above, a light-emitting element in

which an electrode to serve as a cathode is provided on a substrate side may be used. It is to be noted that light generated by recombination of carriers in the layer 202 including the luminescent material is emitted from one or both of the first electrode 201 and the second electrode 203 in the light-emitting element according to the present invention.

[0136]

The above-described light-emitting element according to the present invention shows less decrease in luminance over emission time, and shows a favorable lifetime.

10 [0137]

[Embodiment mode 3]

In Embodiment mode 3, a light-emitting element using an organometallic complex according to the present invention is manufactured over a substrate 300 composed of glass, quartz, a metal, a bulk semiconductor, transparent plastics, a flexible substrate, or the like. By manufacturing a plurality of light-emitting elements using the organometallic complex according to the present invention over a substrate, a passive matrix light-emitting device can be manufactured. In addition, other than a substrate composed of glass, quartz, transparent plastics, a flexible substrate, or the like, for example, a light-emitting element in contact with a thin film transistor (TFT) array may be manufactured as shown in FIG. 3 where a light-emitting element 313 is manufactured together with TFTs 311 and 312.

[0138]

For the light-emitting element 313, a first electrode 314, a layer 315 including a luminescent material, and a second electrode 316 can be manufactured. Further, a wiring 317 is manufactured to come in contact with the first electrode 314. In this way, an active matrix light-emitting device where driving of a light-emitting element is controlled by a TFT can be manufactured. It is to be noted that the structures of the TFTs are not particularly limited. For example, a staggered TFT and an inversely staggered TFT may be used. In addition, the degree of crystallinity of a semiconductor layer forming the TFT is not particularly limited, either. A crystalline semiconductor

layer and an amorphous semiconductor layer may be used.

[0139]

[Embodiment mode 4]

5 The example of a light-emitting element using an organometallic complex according to the present invention as a luminescent material will be described with reference to FIG. 4.

[0140]

10 FIG. 4 shows a light-emitting element that has a light-emitting layer 413 between a first electrode 401 and a second electrode 402. In the light-emitting layer 413, an organometallic complex including a structure represented by any one of the general formulas (1) to (4) according to the present invention or an organometallic complex represented by any one of the general formulas (5) to (8) according to the present invention is included.

15 [0141]

 In this light-emitting element, a hole injected from the first electrode 401 and an electron injected from the second electrode 402 are recombined in the light-emitting layer 413 to bring the organometallic complex according to the present invention to an excited state. Then, light is emitted when the organometallic complex according to the present invention in the excited state returns to the ground state. As just described, the organometallic complex according to the present invention serves as a luminescent material. It is to be noted that the first electrode 401 and the second electrode 402 respectively serve as an anode and a cathode in the light-emitting element in the present embodiment mode.

25 [0142]

 Here, the light-emitting layer 413 is not particularly limited. However, it is preferable that the light-emitting layer 413 be a layer in which the organometallic complex according to the present invention is included so as to be dispersed in a layer composed of a material that has a larger energy gap than the organometallic complex has. This makes it possible to prevent quenching of luminescence from the

30

organometallic complex according to the present invention due to the concentration. It is to be noted that an energy gap indicates an energy gap between a LUMO level and a HOMO level.

[0143]

5 The material to be used for dispersing the organometallic complex according to the present invention is not particularly limited. However, carbazole derivatives such as 4, 4' - bis (N - carbazolyl) - biphenyl (abbreviation: CBP) and 4, 4', 4'' - tris (N - carbazolyl) - triphenylamine (abbreviation: TCTA) and metal complexes such as bis [2 - (2' - hydroxyphenyl) - pyridinato] zinc (abbreviation: Znpp₂), bis [2 - (2' - hydroxyphenyl) - benzoxazolato] zinc (abbreviation: ZnBOX), and tris (8 - quinolinolato) aluminum (abbreviation: Alq₃) are preferable in addition to compounds having an arylamine skeleton such as 2, 3 - bis (4 - diphenylaminophenyl) quinoxaline (abbreviation: TPAQn) and 4, 4' - bis [N - (1 - naphthyl) - N - phenylamino] - biphenyl (abbreviation: α -NPD).

15 [0144]

It is to be noted that it is preferable to be a light-emitting element particularly using, among the organometallic complexes, an organometallic complex having an electron-withdrawing group such as a halogen group, a haloalkyl group, or a cyano group as a luminescent material. This makes it possible to obtain a light-emitting element that is excellent in chromaticity and quantum efficiency.

[0145]

In addition, a fluoro group among halogen groups and a trifluoromethyl group among haloalkyl groups are particularly preferable. By using an organometallic complex having any of these groups as a luminescent material, a light-emitting element that is high in recombination efficiency can be obtained.

[0146]

Although the first electrode 401 is not particularly limited, it is preferable that the first electrode 401 be formed by using a material that has a larger work function when the first electrode 401 functions as an anode as in the present embodiment mode. Specifically, in addition to indium tin oxide (ITO), indium tin oxide including silicon

oxide, and indium oxide including zinc oxide at 2 to 20 %, gold (Au), platinum (Pt), nickel (Ni), tungsten (W), chromium (Cr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), palladium (Pd), and the like can be used. The first electrode 401 can be formed by, for example, sputtering or evaporation.

5 [0147]

In addition, although the second electrode 402 is not particularly limited, it is preferable that the second electrode 402 be formed by using a material that has a smaller work function when the second electrode 402 functions as a cathode as in the present embodiment mode. Specifically, aluminum containing an alkali metal or an
10 alkali-earth metal such as lithium (Li) or magnesium, and the like can be used. The second electrode 402 can be formed by, for example, sputtering or evaporation.

[0148]

Further, in order to extract emitted light to the outside, it is preferable that any one or both of the first electrode 401 and the second electrode 402 be an electrode
15 composed of a material such as indium tin oxide or an electrode formed to be several to several tens nm in thickness so that visible light can be transmitted.

[0149]

In addition, a hole transporting layer 412 may be provided between the first electrode 401 and the light-emitting layer 413 as shown in FIG. 4. Here, a hole
20 transporting layer is a layer that has a function of transporting holes injected from the first electrode 401 to the light-emitting layer 413. By providing the hole transporting layer 412 to keep the first electrode 401 away from the light-emitting element 413 in this way, quenching of luminescence due to a metal can be prevented.

[0150]

25 The hole transporting layer 412 is not particularly limited, and it is possible to use a layer formed with the use of, for example, an aromatic amine compound (that is, compound including a bond of a benzene ring-nitrogen) such as 4, 4' - bis [N - (1 - naphthyl) - N - phenyl - amino] - biphenyl (abbreviation: α -NPD), 4, 4' - bis [N - (3 - methylphenyl) - N - phenyl - amino] - biphenyl (abbreviation: TPD), 4, 4', 4'' - tris (N,
30 N - diphenyl - amino) - triphenylamine (abbreviation: TDATA), or 4, 4', 4'' - tris [N - (3

- methylphenyl) - N - phenyl - amino] - triphenylamine (abbreviation: MTDATA).

[0151]

In addition, the hole transporting layer 412 may be a layer that has a multilayer structure formed by combining two or more layers each including the material
5 mentioned above.

[0152]

Further, an electron transporting layer 414 may be provided between the second electrode 402 and the light-emitting layer 413 as shown in FIG. 4. Here, an electron transporting layer is a layer that has a function of transporting electrons
10 injected from the second electrode 402 to the light-emitting layer 413. By providing the electron transporting layer 414 to keep the second electrode 402 away from the light-emitting element 413 in this way, quenching of luminescence due to a metal can be prevented.

[0153]

15 The electron transporting layer 414 is not particularly limited, and it is possible to use a layer formed with the use of, for example, a metal complex including a quinoline skeleton or a benzoquinoline skeleton such as tris (8 - quinolinolato) aluminum (abbreviation: Alq₃), tris (4 - methyl - 8 - quinolinolato) aluminum (abbreviation: Almq₃), bis (10 - hydroxybenzo [h] quinolinato) beryllium (abbreviation:
20 BeBq₂), or bis (2 - methyl - 8 - quinolinolato) - 4 - phenylphenolato - aluminum (abbreviation: BAlq). In addition, a layer formed with the use of, for example, a metal complex including a oxazole-based ligand or a thiazole-based ligand such as bis [2 - (2' - hydroxyphenyl) - benzoxazolato] zinc (abbreviation: ZnBOX) or bis [2 - (2' - hydroxyphenyl) - benzothiazolato] zinc (abbreviation: Zn(BTZ)₂), may be used.
25 Further, a layer formed with the use of 2 - (4 - biphenyl) - 5 - (4 - tert - butylphenyl) - 1, 3, 4 - oxadiazole (abbreviation: PBD), 1, 3 - bis [5 - (p - tert - butylphenyl) - 1, 3, 4 - oxadiazole - 2 - yl] benzene (abbreviation: to as OXD-7), 3 - (4 - tert - butylphenyl) - 4 - phenyl - 5 - (4 - biphenyl) - 1, 2, 4 - triazole (abbreviation: TAZ), 3 - (4 - tert - butylphenyl) - 4 - (4 - ethylphenyl) - 5 - (4 - biphenyl) - 1, 2, 4 - triazole
30 (abbreviation: p-EtTAZ), bathophenanthroline (abbreviation: BPhen), bathocuproin

(abbreviation: BCP) or the like may be used.

[0154]

In addition, the electron transporting layer 414 may be a layer that has a multilayer structure formed by combining two or more layers each including the material mentioned above.

[0155]

Further, a hole injecting layer 411 may be provided between the first electrode 401 and the hole transporting layer 412 as shown in FIG. 4. Here, a hole injecting layer is a layer that has a function of assisting injection of holes from an electrode to serve as an anode to the hole transporting layer 412. It is to be noted that injection of holes into a light-emitting layer may be assisted by providing a hole injecting layer between an electrode to serve as an anode and the light-emitting layer when no hole transporting layer is particularly provided.

[0156]

The hole injecting layer 411 is not particularly limited, and it is possible to use a layer formed with the use of, for example, a metal oxide such as molybdenum oxide (MoOx), vanadium oxide (VOx), ruthenium oxide (RuOx), tungsten oxide (WOx), manganese oxide (MnOx). In addition, the hole injecting layer 411 can be formed with the use of a phthalocyanine compound such as phthalocyanine (abbreviation: H₂Pc) or copper phthalocyanine (abbreviation: CuPc), a poly(ethylenedioxythiophene)/poly(styrene sulfonate) aqueous solution (PEDOT/PSS), or the like.

[0157]

Further, an electron injecting layer 415 may be provided between the second electrode 402 and the electron transporting layer 414 as shown in FIG. 4. Here, an electron injecting layer is a layer that has a function of assisting injection of electrons from an electrode to serve as a cathode to the electron transporting layer 414. It is to be noted that injection of electrons into a light-emitting layer may be assisted by providing an electron injecting layer between an electrode to serve as a cathode and the light-emitting layer when no electron transporting layer is particularly provided.

[0158]

The electron injecting layer 415 is not particularly limited, it is possible to use a layer formed with the use of, for example, a compound of an alkali metal or an alkali-earth metal such as lithium fluoride (LiF), cesium fluoride (CsF), or calcium fluoride (CaF₂). In addition, a layer in which a highly electron transporting material such as Alq₃ or 4, 4 - bis (5 - methylbenzoxazol - 2 - yl) stilbene (abbreviation: BzOS) is mixed with an alkali metal or an alkali-earth metal such as magnesium or lithium can also be used as the electron injecting layer 415.

[0159]

In the above-described light-emitting element according to the present invention, each of the hole injecting layer 411, the hole transporting layer 412, the light-emitting layer 413, the electron transporting layer 414, and the electron injecting layer 415 may be formed by any method, for example, evaporation, inkjet, or coating. In addition, the first electrode 401 and the second electrode 402 may be formed by any method, for example, sputtering or evaporation.

[0160]

The above-described light-emitting element according to the present invention is capable of providing red luminescence that is excellent in chromaticity since the organometallic complex according to the present invention is used. In addition, the light-emitting element according to the present invention is excellent in luminous efficiency since phosphorescence can be emitted. Further, a light-emitting element including a layer in which an organometallic complex according to the present invention is dispersed in a layer composed of a quinoxaline derivative particularly emits light efficiently.

[0161]

[Embodiment mode 5]

A light-emitting element according to the present invention may have a plurality of light-emitting layers. For example, white light can be obtained by providing a plurality of light-emitting layers and mixing luminescence from respective

light-emitting layers. In the present embodiment mode, examples of a light-emitting element that has a plurality of light-emitting layers will be described with reference to FIGS. 5 and 6.

[0162]

5 In FIG. 5, a first light-emitting layer 513 and a second light-emitting layer 515 are provided between a first electrode 501 and a second electrode 502. It is preferable to provide a partition layer 514 between the first light-emitting layer 513 and the second light-emitting layer 515.

[0163]

10 When a voltage is applied so that the potential of the second electrode 502 is higher than the potential of the first electrode 501, current flows between the first electrode 501 and the second electrode 502, and a hole and an electron are recombined in the first light-emitting layer 513, the second light-emitting layer 515, or the partition layer 514. Generated excitation energy transfers to both the first light-emitting layer 513 and the second light-emitting layer 515 through the partition layer 514, and a first
15 luminescent material included in the first light-emitting layer 513 and a second luminescent material included in the second light-emitting layer 515 are excited. Then, light is emitted when the excited first and second luminescent materials return to the respective ground states.

20 [0164]

The first light-emitting layer 513 includes a luminescent material typified by a fluorescent material such as perylene, 2, 5, 8, 11 - tetra - tert - butylperylene (TBP), 4, 4' - bis (2, 2 - diphenylvinyl) biphenyl (DPVBi), 4, 4' - bis [2 - (N - ethylcarbazole - 3 - yl) vinyl] biphenyl (BCzVBi), bis (2 - methyl - 8 - quinolinolato) - 4 - phenylphenolato -
25 aluminum (BALq), or bis (2 - methyl - 8 - quinolinolato) - chlorogallium (Gamq₂Cl), or a phosphorescent material such as bis [2 - (3', 5' - bis (trifluoromethyl) phenyl) pyridinato - N, C^{2'}] iridium (III) picolate (Ir(CF₃ppy)₂(pic)), bis [2 - (4', 6' - difluorophenyl) pyridinato - N, C^{2'}] iridium (III) acetylacetonate (FIr(acac)), or bis [2 - (4', 6' - difluorophenyl) pyridinato - N, C^{2'}] iridium (III) picolate (FIr(pic)), from
30 which luminescence with a peak at 450 to 510 nm in an emission spectrum can be

obtained.

[0165]

In addition, the second light-emitting layer 515 includes an organometallic complex according to the present invention to serve as a luminescent material, and
5 luminescence with a peak at 580 to 680 nm in an emission spectrum can be obtained from the second light-emitting layer 515. Then, the luminescent color of luminescence from the first light-emitting layer 513 and the luminescent color of luminescence from the second light-emitting layer 515 are emitted to the outside through one or both of the first electrode 501 and the second electrode 502. Each luminescence emitted to the
10 outside is visually mixed to be visually recognized as white light.

[0166]

It is preferable that the first light-emitting layer 513 be a layer in which a luminescent material that is capable of providing luminescence of 450 to 510 nm is included to be dispersed in a layer composed of a material (first host) that has a larger
15 energy gap than the luminescent material, or a layer composed of a luminescent material that is capable of providing luminescence of 450 to 510 nm. As the first host, in addition to α -NPD, CBP, TCTA, Znpp₂, and ZnBOX mentioned above, 9, 10 - di (2 - naphthyl) anthracene (abbreviation: DNA), 9, 10 - di (2 - naphthyl) - 2 - tert - butylanthracene (abbreviation: t-BuDNA), and the like can be used. Further, it is
20 preferable that the second light-emitting layer 515 be a layer in which an organometallic complex according to the present invention is included to be dispersed in a layer composed of a material (second host) that has a larger energy gap than the organometallic complex according to the present invention. As the second host, TPAQn, α -NPD, CBP, TCTA, Znpp₂, ZnBOX, Alq₃, and the like can be used. Further,
25 it is preferable that the partition layer 514 be formed so that energy generated in the first light-emitting layer 513, the second light-emitting layer 515, or the partition layer 514 can transfer to both the first light-emitting layer 513 and the second light-emitting layer 515, and be formed to have a function for preventing energy from transferring only one of the first light-emitting layer 513 and the second light-emitting layer 515.
30 Specifically, the partition layer 514 can be formed with the use of TPAQn, α -NPD, CBP,

TCTA, Znpp₂, ZnBOX, or the like. As described above, by providing the partition layer 514, it is possible to prevent a problem that stronger emission strength from only one of the first light-emitting layer 513 and the second light-emitting layer 515 makes it impossible to obtain white light.

5 [0167]

In the present embodiment mode, the luminescent material included in each of the first light-emitting layer 513 and the second light-emitting layer 515 is not particularly limited. However, as in the present embodiment mode, when an organometallic complex according to the present invention is used for a light-emitting
10 layer (the second electrode 502 in the present embodiment mode) that is closer to an electrode to serve as an anode (the second light-emitting layer 515 in the present embodiment mode), the luminescent material included in each layer is made to emit light more efficiently.

[0168]

15 In addition, in the present embodiment mode, the light-emitting layer in which the two light-emitting layers are provided as shown in FIG. 5 is described. However, the number of light-emitting layer is not to be considered limited to two, and for example, three light-emitting layers may be used. Further, luminescence from each light-emitting layer may be combined to be visually recognized as white light.

20 [0169]

Furthermore, an electron transporting layer 512 may be provided between the first light-emitting layer 513 and the first electrode 501 as shown in FIG. 5, an electron injecting layer 511 may be provided between the electron transporting layer 512 and the first electrode 501 in addition to the electron transporting layer 512, a hole transporting
25 layer 516 may be provided between the second light-emitting layer 515 and the second electrode 502 as shown in FIG. 5, and a hole injecting layer 517 may be provided between the hole transporting layer 516 and the second electrode 502.

[0170]

In addition to the light-emitting element described with reference to FIG. 5, a
30 light-emitting element shown in FIG. 6 may be used.

[0171]

The light-emitting element shown in FIG. 6 has a first light-emitting layer 613 and a second light-emitting layer 618 between a first electrode 601 and a second electrode 602. Between the first light-emitting layer 613 and the second light-emitting layer 618, a first layer 615 and a second layer 616 are provided.

[0172]

The first layer 615 is a layer that generates holes, and the second layer 616 is a layer that generates electrons. When a voltage is applied so that the potential of the second electrode 602 is higher than the potential of the first electrode 601, an electron injected from the first electrode 601 and a hole injected from the first layer 615 are recombined in the first light-emitting layer 613, and a luminescent material included in the first light-emitting layer 613 emits light. Further, a hole injected from the second electrode 602 and an electron injected from the second layer 616 are recombined in the second light-emitting layer 618, and a luminescent material included in the second light-emitting layer 618 emits light.

[0173]

In the first light-emitting layer 613, an organometallic complex according to the present invention is included so as to serve as a luminescent material, and luminescence with a peak at 580 to 680 nm in an emission spectrum can be obtained from the first light-emitting layer 613. In addition, the second light-emitting layer 618 includes a luminescent material typified by a fluorescent material such as perylene, TBP, DPVBi, BCzVBi, BAlq, or Gamq₂Cl, or a phosphorescent material such as Ir(CF₃ppy)₂(pic), FIr(acac), or FIr(pic), from which luminescence with a peak at 450 to 510 nm in an emission spectrum can be obtained. Luminescence from the first light-emitting layer 613 and the second light-emitting layer 618 is emitted from one or both of the first electrode 601 and the second electrode 602. Then, the luminescence from each light-emitting layer is visually mixed to be visually recognized as white light.

[0174]

In the first light-emitting layer 613, it is preferable that the organometallic complex according to the present invention be included to be dispersed in the second host

as described above. It is also preferable that the second light-emitting layer 618 be formed in the same way as the first light-emitting layer 513 described above.

[0175]

It is preferable that the first layer 615 be a layer in which a highly hole transporting material rather than an electron transporting material includes a material that shows an electron-accepting property to the highly hole transporting material. As the highly hole transporting material, the same material as a material that is used for forming a hole transporting layer may be used. In addition, as the material that shows an electron-accepting property to the highly hole transporting material, molybdenum oxide, vanadium oxide, 7, 7, 8, 8 - tetracyanoquinodimethane (abbreviation: TCNQ), 2, 3, 5, 6 - tetrafluoro - 7, 7, 8, 8 - tetracyanoquinodimethane (abbreviation: F4-TCQN), and the like can be used.

[0176]

It is preferable that the second layer 616 be a layer in which a highly electron transporting material rather than a hole transporting material includes a material that shows an electron-donating property to the highly electron transporting material. As the highly electron transporting material, the same material as a material that is used for forming an electron transporting layer may be used. In addition, as the material that shows an electron-donating property to the highly electron transporting material, alkali metals such as lithium and cesium, alkali-earth metals such as magnesium and calcium, rare-earth metals such as erbium and ytterbium, and the like can be used.

[0177]

Furthermore, an electron transporting layer 612 may be provided between the first light-emitting layer 613 and the first electrode 601 as shown in FIG. 6, an electron injecting layer 611 may be provided between the electron transporting layer 612 and the first electrode 601, a hole transporting layer 614 may be provided between the first light-emitting layer 613 and the first layer 615, a hole transporting layer 619 may be provided between the second light-emitting layer 618 and the second electrode 602, a hole injecting layer 620 may be provided between the hole transporting layer 619 and the second electrode 602, and an electron transporting layer 617 may be provided

between the second light-emitting layer 618 and the second layer 616 .

[0178]

In addition, in the present embodiment mode, the light-emitting layer in which the two light-emitting layers are provided as shown in FIG. 6 is described. However, the number of the light-emitting layer is not to be considered limited to two, and for example, three light-emitting layers may be used. Further, luminescence from each light-emitting layer may be combined to be visually recognized as white light.

[0179]

10 [Embodiment mode 6]

The example of a light-emitting element using an organometallic complex according to the present invention as a sensitizer will be described with reference to FIG. 7.

[0180]

15 FIG. 7 shows a light-emitting element that has a light-emitting layer 713 between a first electrode 701 and a second electrode 702. The light-emitting layer 713 includes an organometallic complex including a structure represented by any one of the general formulas (1) to (4) according to the present invention or an organometallic complex represented by any one of the general formulas (5) to (8) according to the present invention, and a fluorescent material that is capable of providing luminescence of a longer wavelength than organometallic complex according to the present invention.

[0181]

In this light-emitting element, a hole injected from the first electrode 701 and an electron injected from the second electrode 702 are recombined in the light-emitting layer 713 to bring the fluorescent material into an excited state. Then, light is emitted when the fluorescent material in the excited state returns to the ground state. In this case, the organometallic complex acts as a sensitizer for the fluorescent material to increase the number of singlet excited states of the fluorescent material. As described above, a light-emitting element that is excellent in luminous efficiency can be obtained by using an organometallic complex according to the present invention as a sensitizer.

25

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It is to be noted that the first electrode 701 and the second electrode 702 respectively serve as an anode and a cathode in the light-emitting element in the present embodiment mode.

[0182]

5 Here, the light-emitting layer 713 is not particularly limited. However, it is preferable that the light-emitting layer 713 be a layer in which the organometallic complex according to the present invention and the fluorescent material are included so as to be dispersed in a layer composed of a material that has a larger energy gap than the organometallic complex has. This makes it possible to prevent quenching of
10 luminescence from the organometallic complex according to the present invention due to the concentration. It is to be noted that an energy gap indicates an energy gap between a LUMO level and a HOMO level.

[0183]

Here, although the fluorescent material is not particularly limited, compounds
15 that show red to infrared luminescence such as magnesium phthalocyanine and phthalocyanine are preferable.

[0184]

In addition, the material to be used for dispersing the organometallic complex according to the present invention and the fluorescent material is not particularly limited,
20 and the materials that can be used for dispersing the organometallic complex according to the present invention, which are described in Embodiment mode 3, and the like can be used.

[0185]

In addition, the first electrode 701 or the second electrode 702 is not
25 particularly limited, and the same materials as those for the first electrode 401 and second electrode 402 described in Embodiment mode 4, can be used.

[0186]

Furthermore, a hole injecting layer 711, a hole transporting layer 712, and the like may be provided between the first electrode 701 and the light-emitting layer 713 as
30 shown in FIG. 7, and an electron transporting layer 714, an electron injecting layer 715,

and the like may be provided also between the second electrode 702 and the light-emitting layer 713.

[0187]

For the hole injecting layer 711, the hole transporting layer 712, the electron
5 transporting layer 714, and the electron injecting layer 715, the same materials as those
for the hole injecting layer 411, the hole transporting layer 412, the electron transporting
layer 414, and the electron injecting layer 415 described in Embodiment mode 4, can be
used, respectively. In addition, another functional layer that has a different function
from the hole injecting layer 711, the hole transporting layer 712, the electron
10 transporting layer 714, and the electron injecting layer 715 may be provided.

[0188]

The light-emitting element described above can be obtained by using an
organometallic complex according to the present invention as a sensitizer.

15 [0189]

[Embodiment mode 7]

Since a light-emitting element including an organometallic complex according
to the present invention shows a favorable luminescent color, a light-emitting device
that has a function of displaying favorable images in terms of color can be obtained by
20 using the light-emitting element according to the present invention for a pixel. Further,
since the light-emitting element according to the present invention is capable of
emitting light efficiently, a light-emitting device with low power consumption can be
obtained by using the light-emitting element according to the present invention for a
pixel or the like.

25 [0190]

In the present embodiment mode, a circuit configuration and driving method of
a light-emitting device that has a display function will be described with reference to
FIGS. 8 to 11.

[0191]

30 FIG. 8 is an overhead schematic view of a light-emitting device to which the

present invention is applied. In FIG 8, a pixel portion 811, a source signal line driver circuit 812, a writing gate signal line driver circuit 813, and an erasing gate signal line driver circuit 814 are provided on a substrate 800. Each of the source signal line driver circuit 812, the writing gate signal line driver circuit 813, and the erasing gate signal line driver circuit 814 is connected to FPC (Flexible Printed Circuit) 801 that is an external input terminal through a group of wirings. Further, each of the source signal line driver circuit 812, the writing gate signal line driver circuit 813, and the erasing gate signal line driver circuit 814 receives signals such as a clock signal, a start signal, and a reset signal from the FPC 801. In addition, a printed wiring board (PWB) 802 is attached to the FPC 801. It is to be noted that it is not always necessary to provide the driver circuit portion on the same substrate on which the pixel portion 811 is provided as described above. For example, the driver circuit portion may be provided outside the substrate by using a TCP that has an IC chip on an FPC on which a wiring pattern is formed.

15 [0192]

In the pixel portion 811, a plurality of source signal lines extending in columns is arranged in rows, current supply lines are arranged to line in rows, and a plurality of gate signal lines extending in rows is arranged to line in columns. Further, in the pixel portion 811, a plurality of circuits each including a light-emitting element is arranged.

20 [0193]

FIG. 9 is a diagram showing a circuit for operating one pixel. The circuit shown in FIG. 9 includes a first transistor 901, a second transistor 902, and a light-emitting element 903.

[0194]

25 Each of the first transistor 901 and the second transistor 902 is a three-terminal element including a gate electrode, a drain region, and a source region, and including a channel region between the drain region and the source region. Here, since a source region and a drain region are switched with each other in accordance with a structure or operating conditions of a transistor, it is difficult to identify which one is the drain region or the source region. Consequently, regions that serve as a source or a drain are

30

referred to as first and second electrodes in the present embodiment mode.

[0195]

A gate signal line 911 and a writing gate signal line driver circuit 913 are provided so as to be electrically connected or unconnected by a switch 918, the gate
5 signal line 911 and an erasing gate signal line driver circuit 914 are provided so as to be electrically connected or unconnected by a switch 919, and a source signal line 912 is provided so as to be electrically connected to any one of a source signal line driver circuit 915 and a power source 916 by a switch 920. Further, the first transistor 901
10 has a gate electrically connected to the gate signal line 911, a first electrode electrically connected to the source signal line 912, and a second electrode electrically connected to a gate electrode of the second transistor 902. The second transistor 902 has a first electrode electrically connected to a current supply line 917 and a second electrode electrically connected to one electrode included in the light-emitting element 903. It is
15 to be noted that the switch 918 may be included in the writing gate signal line driver circuit 913, the switch 919 may be included in the erasing gate signal line driver circuit 914, and the switch 920 may be included in the source signal line driver circuit 915.

[0196]

In addition, arrangement of a transistor, a light-emitting element, and the like is not particularly limited. For example, arrangement shown in a top view of FIG. 10 can
20 be employed. In FIG. 10, a first transistor 1001 has a first electrode connected to a source signal line 1004 and a second electrode connected to a gate electrode of a second transistor 1002. Further, the second transistor 1002 has a first electrode connected to a current supply line 1005 and a second electrode connected to an electrode 1006 of a light-emitting element. A portion of a gate signal line 1003 serves as a gate electrode
25 of the first transistor 1001.

[0197]

Next, a driving method will be described. FIG. 11 is a diagram illustrating operation per frame with time. In FIG. 11, the lateral direction indicates passage of time, and the vertical direction indicates ordinal numbers of gate signal lines.

30 [0198]

When a light-emitting device according to the present invention is used to display images, rewrite operation and image display operation for a screen are repeated in a display period. Although the number of rewrites is not particularly limited, it is preferable that the number of rewrites be about 60 times per second so as not to make an image viewer recognize flickers. Here, a period for which rewrite operation and display operation are performed for a screen (one frame) is referred to as one frame period.

[0199]

As shown in FIG. 11, one frame is divided into four sub-frames 1101, 1102, 1103, and 1104 respectively including writing periods 1101a, 1102a, 1103a, and 1104a and retention periods 1101b, 1102b, 1103b, and 1104b. In the retention period, a light-emitting element to which a signal for emitting light is given is made to be in an emitting state. The ratio of the length of the retention period in each sub-frame is first sub-frame 1101 : second sub-frame 1102 : third sub-frame 1103 : fourth sub-frame 1104 = $2^3 : 2^2 : 2^1 : 2^0 = 8 : 4 : 2 : 1$. This makes 4-bit gradation possible. However, the number of bits or the number of gradations is not limited to that described here. For example, eight sub-frames may be provided so as to perform 8-bit gradation.

[0200]

Operation in one frame will be described. First, in the sub-frame 1101, writing operation is sequentially performed for each of the first row to the last row. Accordingly, the start time of the writing period 1101a is different depending on the row. When the writing period 1101a is completed, the row is sequentially moved into the retention period 1101b. In the retention period 1101b, a light-emitting element to which a signal for emitting light is given is made to be in an emitting state. Further, when the retention period 1101b is completed, the row is sequentially moved into the next sub-frame 1102, and writing operation is sequentially performed for each of the first row to the last row as in the case of the sub-frame 1101. The operation described above is repeated to complete the retention period 1104b of the sub-frame 1104. When the operation in the sub-frame 1104 is completed, the row is moved into the next frame. Thus, the total of time for which light is emitted in each sub-frame is emission time for

each light-emitting element in one frame. By varying this emission time with respect to each light-emitting element to have various combinations in one pixel, various different display colors in luminosity and chromaticity can be made.

[0201]

5 As in the sub-frame 1104, when forcible termination of a retention period of a row for which writing is already completed to move into the retention time is required before writing for the last row is completed, it is preferable that an erasing period 1104c be provided after the retention period 1104b and a row be controlled so as to be in a non-emitting state forcibly. Further, the row made to be in the non-emitting state
10 forcibly is kept the non-emitting state for a certain period (this period is referred to as a non-emission period 1104d). Then, immediately after the writing period 1104a of the last row is completed, the rows are sequentially moved into the next writing period (or the next frame), starting from the first row. This makes it possible to prevent the writing period 1104a of the sub-frame 1104 from overlapping with the writing period of
15 the next sub-frame.

[0202]

One horizontal period is divided into two periods, a selection period for inputting an erasing signal to a row and a selection period for inputting image signals to another row, and the signal to be input to the source signal line 912 is switched in
20 accordance with each selection period. According to such an operation method, the retention period 1104b can be made shorter than the time required for writing to all the rows by providing the non-emission period 1104d.

[0203]

Although the sub-frames 1101 to 1104 are arranged in the order of retention
25 period from longest to shortest in the present embodiment mode, the arrangement as in the present embodiment mode is not always necessary. For example, the sub-frames 1101 to 1104 may be arranged in the order of retention period from shortest to longest, or may be arranged in random order. In addition, the sub-frames may be divided further into a plurality of frames. Namely, scanning of the gate signal lines may be
30 performed more than once while giving the same image signal.

[0204]

Now, operation of the circuit shown in FIG. 9 in a writing period and an erasing period will be described.

[0205]

5 First, operation in a writing period will be described. In the writing period, the n -th (n is a natural number) gate signal line 911 is electrically connected to the writing gate signal line driver circuit 913 through the switch 918, and unconnected to the erasing gate signal line driver circuit 914. In addition, the source signal line 912 is electrically connected to the source signal line driver circuit 915 through the switch 920.

10 In this case, a signal is input to the gate of the first transistor 901 connected to the n -th (n is a natural number) gate signal line 911 to turn on the first transistor 901. Then, at this moment, image signals are input simultaneously to the first to last source signal lines 912. It is to be noted that the image signals input from the respective source signal lines 912 are independent of each other. The image signal input from each of

15 the source signal lines 912 is input to the gate electrode of the second transistor 902 through the first transistor 901 connected to the source signal line 912. At this moment, switching of the second transistor 902 is controlled in accordance with the signal input to the second transistor 902. Therefore, depending on the signal input to the gate electrode of the second transistor 902, whether the light-emitting element 903

20 emits light or not is determined. For example, when the second transistor 902 is a p-channel transistor, the light-emitting element 903 is made to emit light by inputting a Low Level signal to the gate electrode of the second transistor 902. On the other hand, when the second transistor 902 is an n-channel transistor, the light-emitting element 903 is made to emit light by inputting a High Level signal to the gate electrode of the second

25 transistor 902.

[0206]

Next, operation in an erasing period will be described. In the erasing period, the n -th (n is a natural number) gate signal line 911 is electrically connected to the erasing gate signal line driver circuit 914 through the switch 919 and unconnected to the

30 wiring gate signal line driver circuit 913. In addition, the source signal line 912 is

electrically connected to the power source 916 through the switch 920. In this case, a signal is input to the gate of the first transistor 901 connected to the n -th (n is a natural number) gate signal line 911 to turn on the first transistor 901. Then, at this moment, erasing signals are input simultaneously to the first to last source signal lines 912. The
5 erasing signal input from each of the source signal lines 912 is input to the gate electrode of the second transistor 902 through the first transistor 901 connected to the source signal line 912. At this moment, current supply from the current supply line 917 to the light-emitting element 903 is blocked in accordance with the signal input to the second transistor 902. Then, the light-emitting element 903 is forcibly made to be
10 in a non-emitting state. For example, when the second transistor 902 is a p-channel transistor, the light-emitting element 903 is made to emit no light by inputting a High Level signal to the gate electrode of the second transistor 902. On the other hand, when the second transistor 902 is an n-channel transistor, the light-emitting element 903 is made to emit no light by inputting a Low Level signal to the gate electrode of the
15 second transistor 902.

[0207]

It is to be noted that, as for the n -th row (n is a natural number), signals for erasing are input by the operation as described above in an erasing period. However, as described above, the other row (referred to as the m -th row (m is a natural number))
20 may be in a writing period while the n -th row is in an erasing period. In such a case, it is necessary to input a signal for erasing to the n -th row and input a signal for writing to the m -th row by using the same source signal line. Therefore, operation described below is preferable.

[0208]

25 Immediately after the n -th light-emitting element 903 is made to emit no light by the operation in the erasing period described above, the gate signal line 911 and the erasing gate signal line driver circuit 914 are made to be unconnected to each other, and the switch 920 is switched to connect the source signal line 912 and the source signal line driver circuit 915. Then, in addition to connecting the source signal line 912 to
30 the source signal line driver circuit 915, the gate signal line 911 is connected to the

writing gate signal line driver circuit 913. Then, a signal is input selectively to the m -th gate signal line 911 from the writing gate signal line driver circuit 913 to turn on the first transistor 901, and signals for writing are input to the first to last source signal lines 912 from the source signal line driver circuit 915. This signal makes the m -th light-emitting element 903 is made to be in an emitting or non-emitting state.

[0209]

Immediately after the writing period for the m -th row is completed as described above, an erasing period for the $(n+1)$ -th row is started. For that purpose, the gate signal line 911 and the writing gate signal line driver circuit 913 are made to be unconnected to each other, and the switch 920 is switched to connect the source signal line 912 and the power source 916. Further, the gate signal line 911, which is unconnected to the writing gate signal line driver circuit 913, is made to be connected to the erasing gate signal line driver circuit 914. Then, a signal is input selectively to the $(n+1)$ -th gate signal line 911 from the erasing gate signal line driver circuit 914 to turn on the first transistor 901, and an erasing signal is input from the power source 916. Immediately after the erasing period for the $(n+1)$ -th row is completed, a writing period for the $(m+1)$ -th row is started. Then, an erasing period and a writing period may be repeated in the same way until an erasing period for the last row is completed.

[0210]

Although the example in which the writing period for the m -th row is provided between the erasing period for the n -th row and the erasing period for the $(n+1)$ -th row is described in the present embodiment mode, the present invention is not limited to this. The writing period for the m -th row may be provided between an erasing period for $(n-1)$ -th row and an erasing period for n -th row.

[0211]

In addition, in the present embodiment mode, the operation in which the erasing gate signal line driver circuit 914 and one gate signal line 911 are made to be unconnected to each other and the writing gate signal line driver circuit 913 and the other gate signal line 911 are made to be connected to each other is repeated as the non-emission period 1104d is provided in the sub-frame 1104. This type of operation

may be performed in a sub-frame in which a non-emission period is not particularly provided.

[0212]

5 [Embodiment mode 8]

One example of cross sections of a light-emitting device including a light-emitting element according to the present invention will be described with reference to FIGS. 12A to 12C.

[0213]

10 In each of FIGS. 12A to 12C, a portion surrounded by a dotted line is a transistor 1211 provided for driving a light-emitting element 1212 according to the present invention. The light-emitting element 1212 is a light-emitting element according to the present invention, which has a layer 1215 in which a hole generation layer, an electron generation layer, and a layer including a luminescent material are
15 stacked between a first electrode 1213 and a second electrode 1214. The first electrode 1213 and a drain of the transistor 1211 are electrically connected to each other by a wiring 1217 running through a first interlayer insulating film 1216 (1216a to 1216c). In addition, the light-emitting element 1212 is separated by a partition layer 1218 from another light-emitting element provided adjacently. A light-emitting device
20 that has this structure according to the present invention is provided over substrate 1210.

[0214]

It is to be noted that the transistor 1211 shown in each of FIGS. 12A to 12C is a top-gate TFT in which a gate electrode is provided on the opposite side of a
25 semiconductor layer as a center from a substrate. However, the structure of the transistor 1211 is not particularly limited. For example, a bottom-gate TFT may be used. In the case of a bottom-gate TFT, a TFT where a protective film is formed on a semiconductor layer that forms a channel (a channel-protection TFT) may be used, or a TFT where a portion of a semiconductor layer that forms a channel is concave (a
30 channel-etch TFT) may be used.

[0215]

In addition, a semiconductor layer forming the transistor 1211 may be either crystalline or amorphous, or alternatively, may be semi-amorphous.

[0216]

5 The following will describe a semi-amorphous semiconductor. The semi-amorphous semiconductor is a semiconductor that has an intermediate structure between amorphous and crystalline (such as single-crystal or polycrystalline) structures and has a third state that is stable in terms of free energy, which includes a crystalline region that has short range order and lattice distortion. Further, a crystal grain from
10 0.5 to 20 nm is included in at least a region in a film of the semi-amorphous semiconductor. A raman spectrum of the semi-amorphous semiconductor has a shift to a lower wavenumber side than 520 cm^{-1} . In X-ray diffraction, diffraction peaks of (111) and (220) due to a Si crystal lattice are observed. Hydrogen or halogen is included at 1 atomic% or more in the semi-amorphous semiconductor to terminate a
15 dangling bond. Therefore, the semi-amorphous semiconductor is also referred to as a micro-crystalline semiconductor. A silicide gas is decomposed by glow discharge (plasma CVD) to form the semi-amorphous semiconductor. As the silicide gas, in addition to SiH_4 , a gas such as Si_2H_6 , SiH_2Cl_2 , SiHCl_3 , SiCl_4 , or SiF_4 can be used. This silicide gas may be diluted with H_2 or with H_2 and one kind or plural kinds of rare
20 gas elements selected from He, Ar, Kr, and Ne, where the dilution ratio is in the range of 2 : 1 to 1000 : 1. The pressure during glow discharge is approximately in the range of 0.1 Pa to 133 Pa, and the power supply frequency is in the range of 1 MHz to 120 MHz, preferably 13 MHz to 60 MHz. The substrate heating temperature may be 300°C or less, preferably 100 to 250°C . It is desirable to control an impurity of an atmospheric
25 constituent such as oxygen, nitrogen, or carbon to have a concentration of $1 \times 10^{20}/\text{cm}^3$ or less as an impurity element in the film, in particular, the oxygen concentration is controlled to be $5 \times 10^{19}/\text{cm}^3$ or less, preferably $1 \times 10^{19}/\text{cm}^3$ or less. Further, a TFT (thin film transistor) using the semi-amorphous semiconductor has a mobility of approximately 1 to $10\text{ m}^2/\text{Vsec}$.

30

[0217]

Further, specific examples of crystalline semiconductors for the semiconductor layer include single-crystal or polycrystalline silicon and silicon-germanium, which may be formed by laser crystallization or may be formed by crystallization with solid-phase growth using an element such as nickel.

5 [0218]

In the case of using an amorphous material, for example, amorphous silicon to form the semiconductor layer, it is preferable that the light-emitting device have a circuit in which the transistor 1211 and the other transistor (a transistor forming the circuit for driving the light-emitting element) are all n-channel transistors. Other than
10 that case, the light-emitting device may have a circuit including one of an n-channel transistor and a p-channel transistor or may have a circuit including both an n-channel transistor and a p-channel transistor.

[0219]

Further, the first interlayer insulating film 1216 may be a multilayer as shown
15 in FIGS. 12A and 12C, or may be a single layer. The first interlayer insulating film 1216a includes an inorganic material such as silicon oxide or silicon nitride, and the first interlayer insulating film 1216b includes a material with self-flatness such as acrylic, siloxane or silicon oxide that can be used in coating deposition. It is to be noted that siloxane has a framework structure formed by the bond between silicon (Si)
20 and oxygen (O), in which an organic group (for example, an alkyl group or an aromatic hydrocarbon group) including at least hydrogen is used as a substituent. As a substituent, a fluoro group may be used, or an organic group including at least hydrogen and a fluoro group may be used as substituents. In addition, the first interlayer insulating film 1216c has a silicon nitride film including argon (Ar). The materials
25 included in the respective layers are not particularly limited, and therefore materials other than the materials mentioned here may be used. Further, a layer including a material other than these materials may be combined. In this way, both of an inorganic material and an organic material, or one of an inorganic material and an organic material may be used to form the first interlayer insulating film 1216.

30 [0220]

As for the partition layer 1218, it is preferable that an edge portion have a shape varying continuously in curvature radius. In addition, a material such as acrylic, siloxane, resist, or silicon oxide is used to form the partition layer 1218. One or both of an inorganic material and an organic material may be used to form the partition layer
5 1218.

[0221]

In each of FIG. 12A and 12C, only the first interlayer insulating film 1216 is provided between the transistor 1211 and the light-emitting element 1212. However, as shown in FIG. 12B, a second interlayer insulating film 1219 (1219a and 1219b) may
10 be provided in addition to the first interlayer insulating film 1216 (1216a and 1216b). In the light-emitting device shown in FIG. 12B, the first electrode 1213 is connected to the wiring 1217 through the second interlayer insulating film 1219.

[0222]

The second interlayer insulating film 1219 may be a multilayer or a single
15 layer in the same way as the first interlayer insulating film 1216. The second interlayer insulating film 1219a includes a material with self-flatness such as acrylic, siloxane, or silicon oxide that can be used in coating deposition. It is to be noted that siloxane has a framework structure formed by the bond between silicon (Si) and oxygen (O), in which an organic group (for example, an alkyl group or an aromatic hydrocarbon group) including at least hydrogen is used as a substituent. As a substituent, a fluoro
20 group may be used, or an organic group including at least hydrogen and a fluoro group may be used as substituents. In addition, the second interlayer insulating film 1219b has a silicon nitride film including argon (Ar). The materials included in the respective layers are not particularly limited, and therefore materials other than the
25 materials mentioned here may be used. Further, a layer including a material other than these materials may be combined. In this way, both of an inorganic material and an organic material, or one of an inorganic material and an organic material may be used to form the second interlayer insulating film 1219.

[0223]

30 In the light-emitting element 1212, in the case where both the first electrode

1213 and the second electrode 1214 are formed by using a light-transmitting material, emitted light can be extracted from both the first electrode 1213 side and the second electrode 1214 side as indicated by outline arrows of FIG. 12A. In the case where only the second electrode 1214 is formed by using a light-transmitting material, emitted light
5 can be extracted from only the second electrode 1214 side as indicated by an outline arrow of FIG. 12B. In this case, it is preferable that the first electrode 1213 include a highly reflective material or that a film composed of a highly reflective material (a reflective film) be provided below the first electrode 1213. In the case where only the first electrode 1213 is formed by using a light-transmitting material, emitted light can be
10 extracted from only the first electrode 1213 side as indicated by an outline arrow of FIG. 12C. In this case, it is preferable that the second electrode 1214 include a highly reflective material or that a reflective film be provided above the second electrode 1214.

[0224]

In addition, the layer 1215 may be stacked so that the light-emitting element
15 1212 operates when a voltage is applied so that the potential of the second electrode 1214 is higher than the potential of the first electrode 1213, or the layer 1215 may be stacked so that the light-emitting element 1212 operates when a voltage is applied so that the potential of the second electrode 1214 is lower than the potential of the first electrode 1213. The transistor 1211 is an n-channel transistor in the former case, and
20 the transistor 1211 is a p-channel transistor in the latter case.

[0225]

As described above, an active light-emitting device in which driving of a light-emitting element is controlled by a transistor is described in the present embodiment mode. However, in addition, the present invention may be applied to a
25 passive light-emitting device in which a light-emitting element is driven without providing an element for driving such as a transistor. Also in the case of a passive light-emitting device, driving with low power consumption is possible when the passive light-emitting device includes a light-emitting element according to the present invention, which operates at a lower driving voltage.

[Embodiments]

[0226]

Base on the embodiment mode, the present invention will be described in more detail below. However, as a matter of course, the present invention is not limited to these embodiments. First, synthesis examples of organometallic complexes for light-emitting elements according to the present invention and properties of the organometallic complexes will be described, and then, the structures of light-emitting elements according to the present invention and manufacturing methods thereof, and an example of a light-emitting device will be described.

10 [0227]

[Embodiment 1: Synthesis Example of Organometallic Complex and Properties thereof]
(Synthesis Example 1)

The present synthesis example is a synthesis example of {2, 3 - bis (4 - fluorophenyl) quinoxalinato} (acetylacetonato) iridium (III) (abbreviation: Ir(Fdpq)₂(acac)) represented by the formula (16).

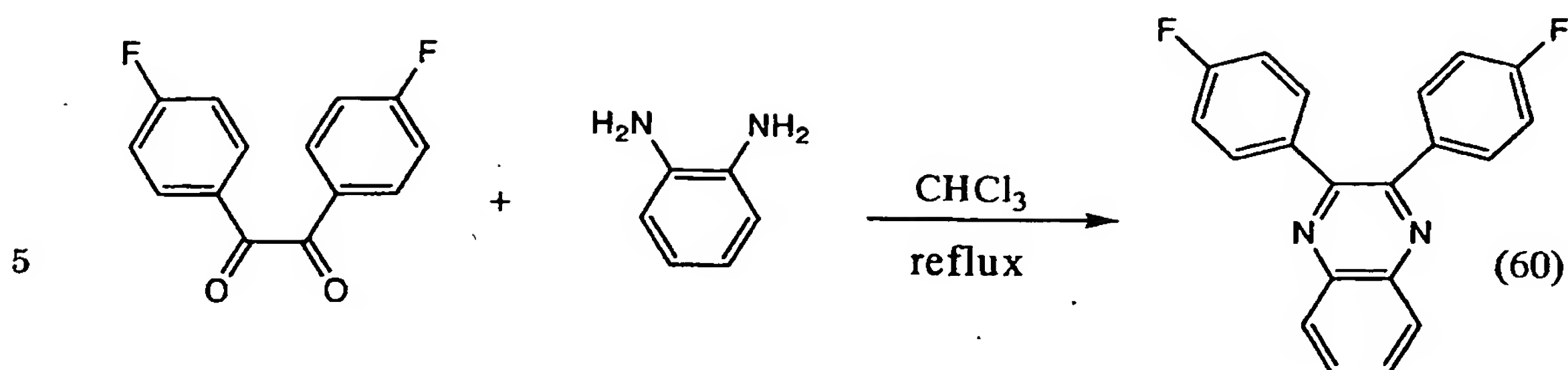
[0228]

<Step 1: Synthesis of Ligand (HFdpq)>

First, 3.71 g of 4, 4' - difluorobenzil and 1.71 g of o-phenylenediamine were stirred on heating in a solvent (200 mL of chloroform) for 6 hours. The reaction solution was cooled to room temperature, washed with HCl (1N) and a saturated aqueous solution of sodium chloride, and dried with magnesium sulfate. The solvent was removed to obtain a ligand HFdpq (2, 3 - bis (4 - fluorophenyl) quinoxaline) (pale yellow powder, yield: 99 %).

[0229]

25 The synthesis scheme and the structure formula of the ligand HFdpq are shown by the following formula (60).



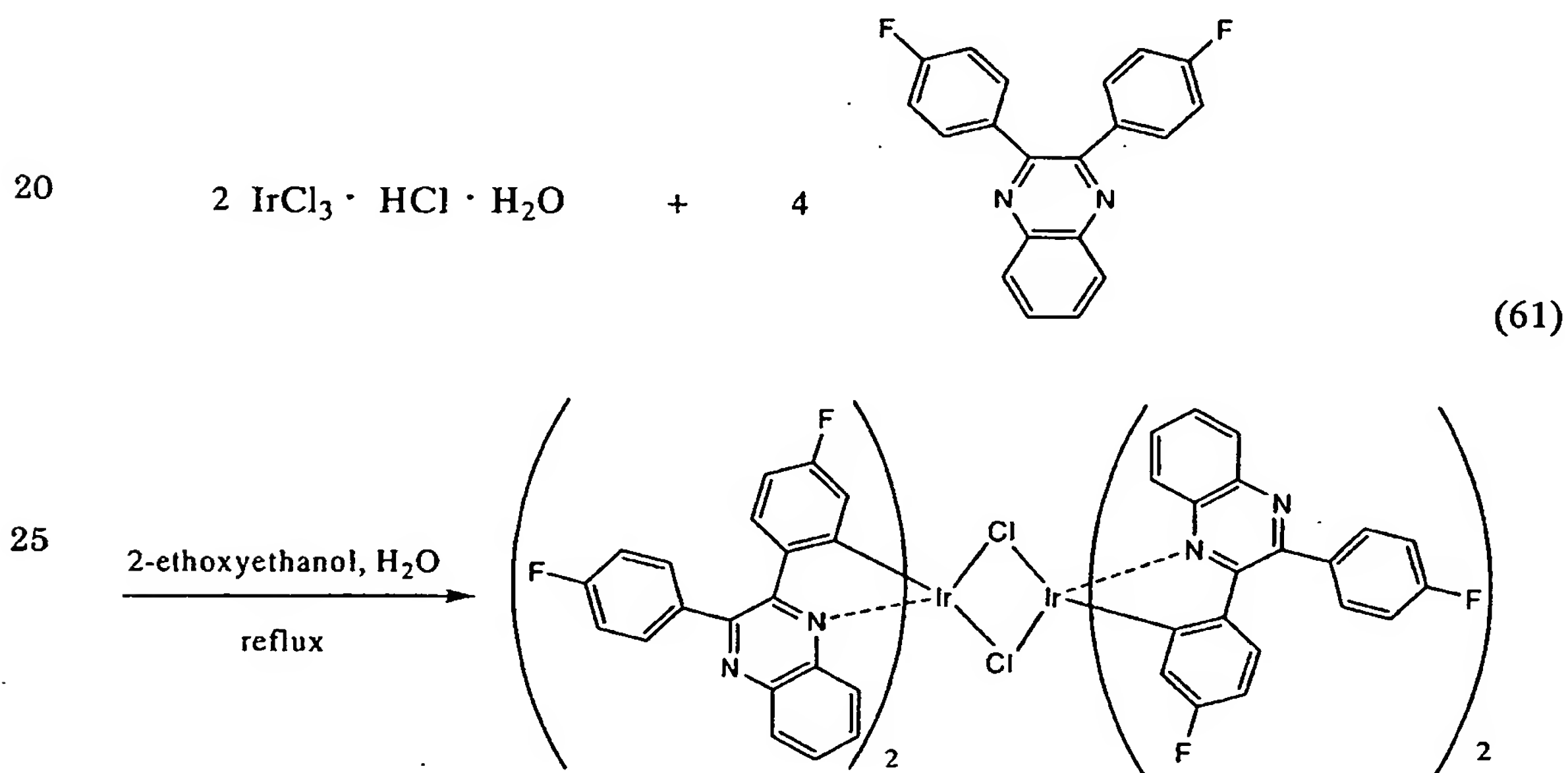
[0230]

<Step 2: Synthesis of Dinuclear Complex $[\text{Ir}(\text{Fdpq})_2\text{Cl}]_2$ >

10 With a mixture of 30 mL of 2 - ethoxyethanol and 10 mL of water as a solvent, 3.61 g of the ligand HFdpq (2, 3 - bis (4 - fluorophenyl) quinoxaline) and 1.35 g of iridium chloride ($\text{IrCl}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$) were mixed, and held at reflux in a nitrogen atmosphere for 17 hours to obtain a dinuclear complex $[\text{Ir}(\text{Fdpq})_2\text{Cl}]_2$ (brown powder, yield: 99 %).

[0231]

15 The synthesis scheme and the structure formula of the dinuclear complex $[\text{Ir}(\text{Fdpq})_2\text{Cl}]_2$ are shown by the following formula (61).



[0232]

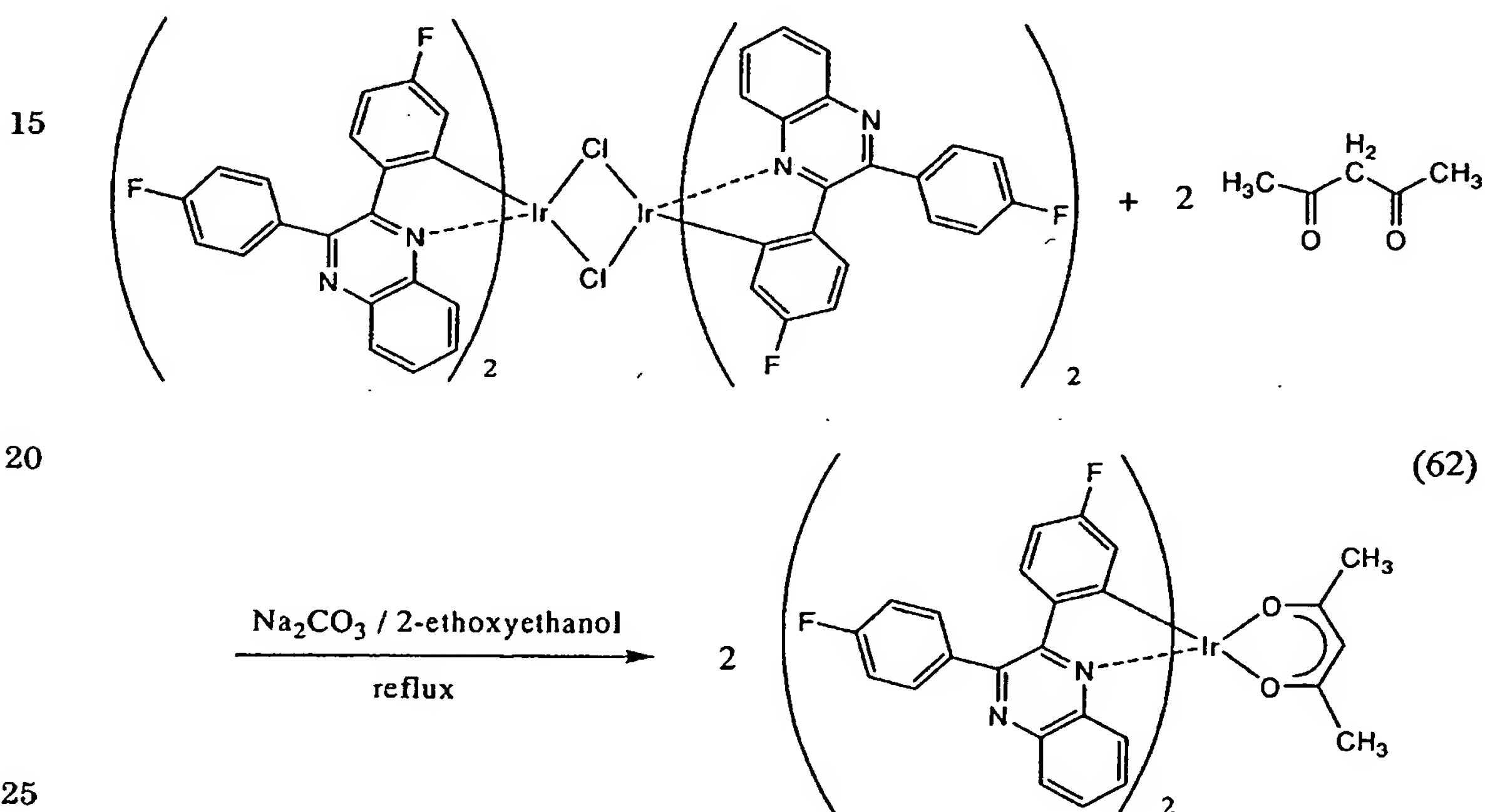
<Step 3: Synthesis of Organometallic Complex $\text{Ir}(\text{Fdpq})_2(\text{acac})$ for Light-Emitting Element according to the Present Invention>

Further, with 30 mL of 2 - ethoxyethanol as a solvent, 2.00 g of the dinuclear complex $[\text{Ir}(\text{Fdpq})_2\text{Cl}]_2$ obtained in Step 2 described above, 0.44 mL of acetylacetone (Hacac), and 1.23 g of sodium carbonate were mixed, and held at reflux in a nitrogen atmosphere for 20 hours to obtain an organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{acac})$ represented by the formula (16) according to the present invention (red powder, yield: 44 %).

10

[0233]

The synthesis scheme is shown by the following formula (62).



[0234]

The result of analysis of the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{acac})$ by nuclear magnetic resonance (^1H -NMR) is as follows.

30

[0235]

¹H-NMR. δ (CDCl₃): 8.20 (d, 2H), 8.11 (d, 2H), 8.01 (brs, 4H), 7.68 (t, 2H), 7.52 (t, 2H), 7.32 (brm, 4H), 7.08 (m, 2H), 6.39 (td, 2H), 6.05 (dd, 2H), 4.71 (s, 1H), 1.62 (s, 6H)

[0236]

5 In addition, measurement of the thermal decomposition temperature T_d of the obtained Ir(Fdpq)₂(acac) was performed by a Thermogravimetry/Differential Thermal Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320) to find $T_d = 365^\circ\text{C}$, and thus, it is determined that the organometallic complex Ir(Fdpq)₂(acac) shows favorable heat resistance.

10 [0237]

Further, FIG. 13 shows an absorption spectrum of the obtained Ir(Fdpq)₂(acac) in dichloromethane and an emission spectrum (Photo Luminescence) thereof. It is to be noted that the emission spectrum was obtained when light with a wavelength of 469 nm was used as excitation light, where the light with the wavelength of 469 nm was
15 extracted by separating light from a halogen lamp with the use of a slit. In FIG. 13, the horizontal axis indicates a wavelength (nm), the left vertical axis indicates absorbance (no unit), and the right vertical axis indicates emission intensity (a.u.: auxiliary unit). As can be seen from FIG. 13, the organometallic complex Ir(Fdpq)₂(acac) according to the present invention has absorption peaks at 232 nm, 284 nm, 371 nm, and 472 nm.
20 In addition, the emission spectrum shows luminescence with an emission peak at 644 nm, and this luminescence was visible as red luminescence.

[0238]

In the case of the obtained Ir(Fdpq)₂(acac), the several absorption peaks are observed. This is absorption unique to an organometallic complex as in the case of an
25 orthometalated complex or the like, and is believed to correspond to singlet MLCT transition, triplet π - π^* transition, triplet MLCT (metal to ligand charge transfer) transition, and the like. In particular, the absorption peak at the longest wavelength side has a broad peak in the visible region, which is considered to be an absorption spectrum unique to triplet MLCT transition. Namely, it is determined that
30 Ir(Fdpq)₂(acac) is a compound capable of direct photoexcitation to an excited triplet

state and intersystem crossing.

[0239]

In addition, a gas including oxygen was injected into a dichloromethane solution including the obtained $\text{Ir}(\text{Fdpq})_2(\text{acac})$, and the emission intensity of $\text{Ir}(\text{Fdpq})_2(\text{acac})$ was examined when the $\text{Ir}(\text{Fdpq})_2(\text{acac})$ with dissolved oxygen was made to produce luminescence. Further, a gas including argon was injected into a dichloromethane solution including the obtained $\text{Ir}(\text{Fdpq})_2(\text{acac})$, and the emission intensity of $\text{Ir}(\text{Fdpq})_2(\text{acac})$ was examined when the $\text{Ir}(\text{Fdpq})_2(\text{acac})$ with dissolved argon was made to produce luminescence. From the result, it was determined that luminescence derived from $\text{Ir}(\text{Fdpq})_2(\text{acac})$ shows the same tendency as luminescence of a phosphorescent material, where the tendency is that the emission intensity is stronger in the case of dissolved argon than dissolved oxygen. Accordingly, luminescence derived from $\text{Ir}(\text{Fdpq})_2(\text{acac})$ is believed to be phosphorescence.

15 [0240]

(Synthesis Example 2)

The present synthesis example is a synthesis example of bis (2, 3 - diphenylquinoxalinato) (acetylacetonato) iridium (III) (abbreviation: $\text{Ir}(\text{dpq})_2(\text{acac})$) represented by the formula (17).

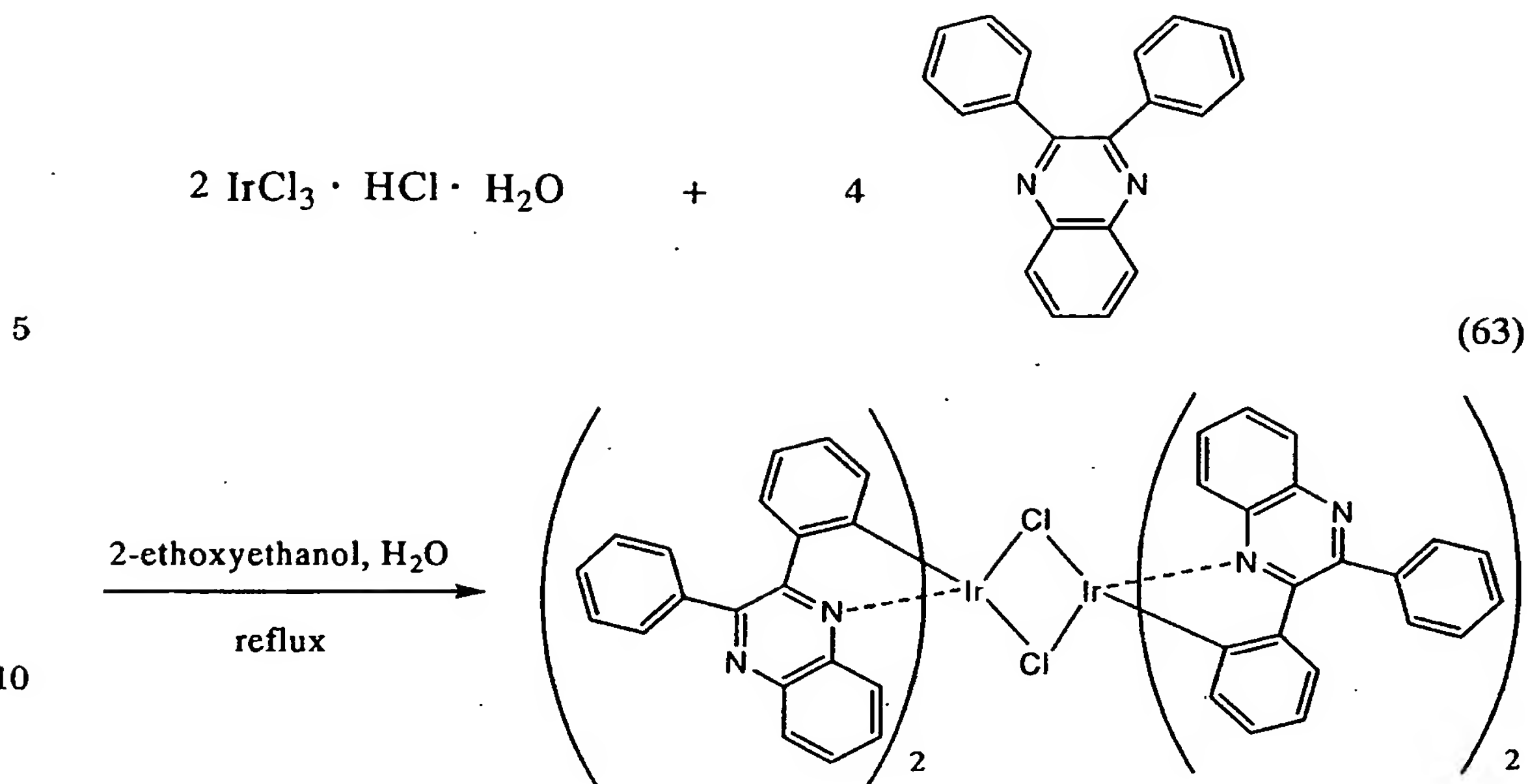
20 [0241]

<Step 1: Synthesis of Dinuclear Complex $[\text{Ir}(\text{dpq})_2\text{Cl}]_2$ >

First, with a mixture of 30 mL of 2 - ethoxyethanol and 10 mL of water as a solvent, 2.36 g of a ligand Hdpq (2, 3 - diphenylquinoxaline) and 1.00 g of iridium chloride ($\text{IrCl}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$) were mixed, and held at reflux in a nitrogen atmosphere for 15 hours to obtain a dinuclear complex $[\text{Ir}(\text{dpq})_2\text{Cl}]_2$ (dark brown powder, yield: 91 %).

[0242]

The synthesis scheme and the structure formula of the dinuclear complex $[\text{Ir}(\text{dpq})_2\text{Cl}]_2$ are shown by the following formula (63).



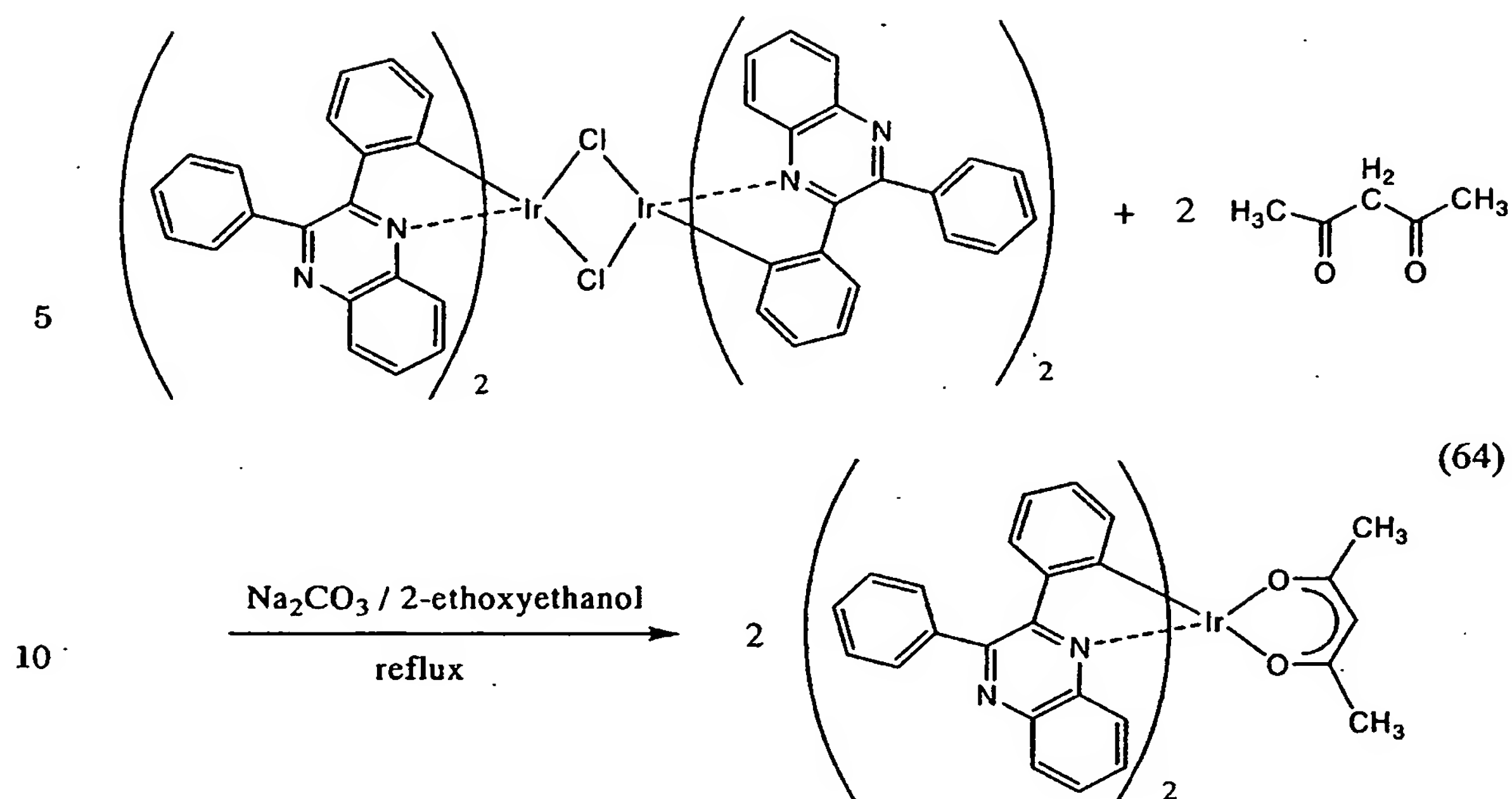
[0243]

15 <Step 2: Synthesis of Organometallic Complex Ir(dpq)₂(acac) according to the Present Invention>

Further, with 30 mL of 2 - ethoxyethanol as a solvent, 1.00 g of the dinuclear complex [Ir(dpq)₂Cl]₂ obtained in Step 1 described above, 0.20 mL of acetylacetone (Hacac), and 0.67 g of sodium carbonate were mixed, and held at reflux in a nitrogen atmosphere for 15 hours. This reaction solution was filtered, and the obtained solution was purified by column chromatography with the use of a dichloromethane solvent. Recrystallization was performed with the use of a dichloromethane/ethanol solvent to obtain an organometallic complex Ir(dpq)₂(acac) according to the present invention (reddish brown powder, yield: 40 %).

[0244]

25 The synthesis scheme is shown by the following formula (64).



[0245]

15 The result of analysis of the organometallic complex $\text{Ir}(\text{dpq})_2(\text{acac})$ by nuclear magnetic resonance (^1H -NMR) is as follows.

[0246]

^1H -NMR. δ (CDCl_3): 8.15 (t, 4H), 7.89 (brs, 4H), 7.79 (t, 2H), 7.69 (m, 8H), 6.94 (d, 2H), 6.57 (t, 2H), 6.48 (t, 2H), 6.33 (d, 2H), 4.81 (s, 1H), 1.64 (s, 6H)

[0247]

20 In addition, measurement of the thermal decomposition temperature T_d of the obtained $\text{Ir}(\text{dpq})_2(\text{acac})$ was performed by a Thermogravimetry/Differential Thermal Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320) to find $T_d = 340^\circ\text{C}$, and thus, it is determined that the organometallic complex $\text{Ir}(\text{dpq})_2(\text{acac})$ shows favorable heat resistance.

25 [0248]

Further, FIG. 14 shows an absorption spectrum of the obtained $\text{Ir}(\text{dpq})_2(\text{acac})$ in dichloromethane and an emission spectrum (PL) thereof. It is to be noted that the emission spectrum was obtained when light with a wavelength of 469 nm was used as excitation light, where the light with the wavelength of 469 nm was extracted by separating light from a halogen lamp with the use of a slit. In FIG. 14, the horizontal

30

axis indicates a wavelength (nm), the left vertical axis indicates absorbance (no unit), and the right vertical axis indicates emission intensity (a.u.). As can be seen from FIG. 14, the obtained organometallic complex Ir(dpq)₂(acac) has absorption peaks at 248 nm, 283 nm, 378 nm, and 479 nm. In addition, the emission spectrum shows luminescence with an emission peak at 687 nm, and this luminescence was visible as deep red luminescence.

[0249]

In the case of the obtained Ir(dpq)₂(acac), the several absorption peaks are observed. This is absorption unique to an organometallic complex as in the case of an orthometalated complex or the like, and is believed to correspond to singlet MLCT transition, triplet π - π^* transition, triplet MLCT transition, and the like. In particular, the absorption peak at the longest wavelength side has a broad peak in the visible region, which is considered to be an absorption spectrum unique to triplet MLCT transition. Namely, it is determined that Ir(dpq)₂(acac) is a compound capable of direct photoexcitation to an excited triplet state and intersystem crossing.

[0250]

In addition, a gas including oxygen was injected into a dichloromethane solution including the obtained Ir(dpq)₂(acac), and the emission intensity of Ir(dpq)₂(acac) was examined when the Ir(dpq)₂(acac) with dissolved oxygen was made to produce luminescence. Further, a gas including argon was injected into a dichloromethane solution including the obtained Ir(dpq)₂(acac), and the emission intensity of Ir(dpq)₂(acac) was examined when the Ir(dpq)₂(acac) with dissolved argon was made to produce luminescence. From the result, it was determined that luminescence derived from Ir(dpq)₂(acac) shows the same tendency as luminescence of a phosphorescent material, where the tendency is that the emission intensity is stronger in the case of dissolved argon than dissolved oxygen. Accordingly, luminescence derived from Ir(dpq)₂(acac) is believed to be phosphorescence.

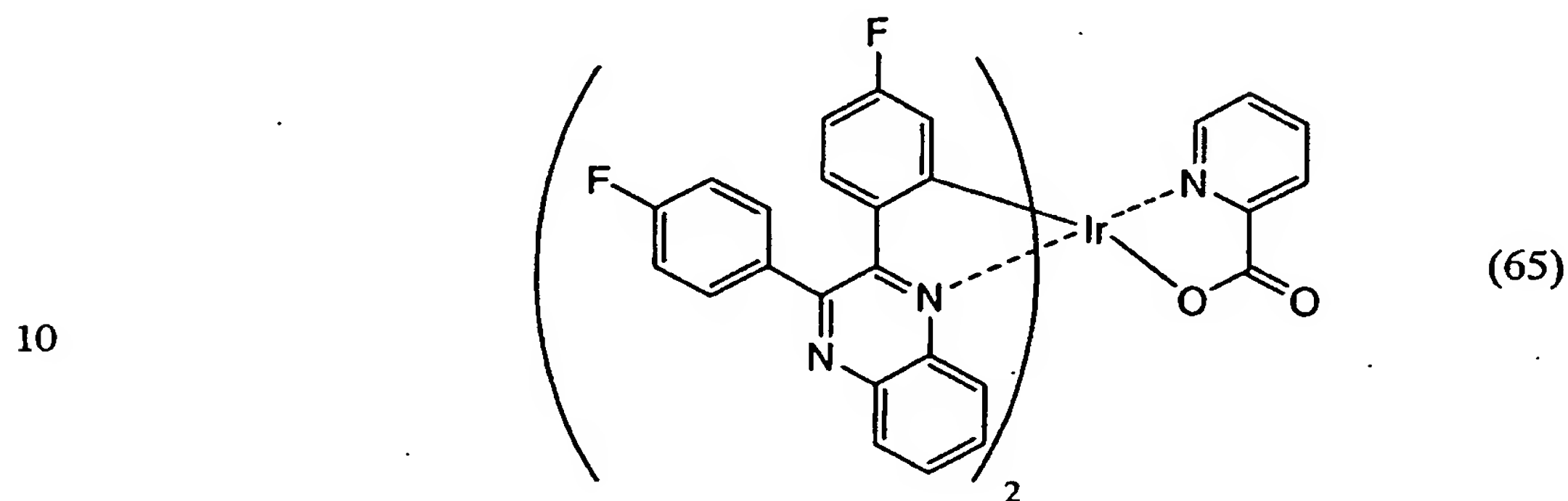
[0251]

(Synthesis Example 3)

The present synthesis example is a synthesis example of {2, 3 - bis (4 - fluorophenyl) quinoxalinato} (picolinato) iridium (III) (abbreviation: Ir(Fdpq)₂(pic)) represented by the following formula (65).

[0252]

5 The structure formula of Ir(Fdpq)₂(pic) is shown by the following formula (65).



[0253]

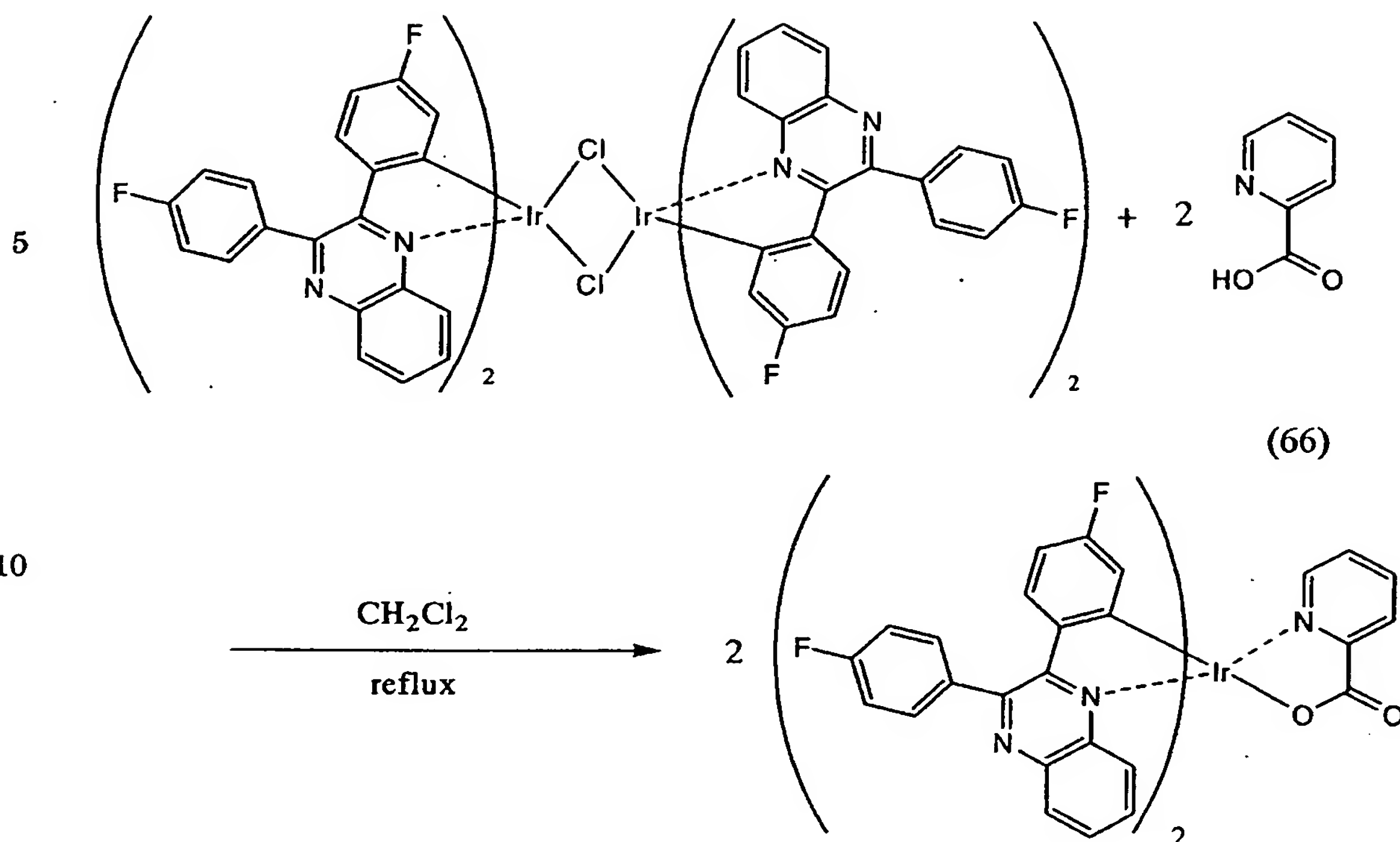
15 First, the dinuclear complex [Ir(Fdpq)₂Cl]₂ obtained in Step 1 of Synthesis Example 1 was used as a material. With 30 mL of dichloromethane as a solvent, 2.87 g of [Ir(Fdpq)₂Cl]₂ and 1.67 g of picolinic acid (Hpic) were mixed, and held at reflux in a nitrogen atmosphere for 16 hours. This reaction solution was filtered to obtain an organometallic complex Ir(Fdpq)₂(pic) (red powder, yield: 56 %)

[0254]

20 The synthesis scheme is shown by the following formula (66).

25

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[0255]

The result of analysis of the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{pic})$ by nuclear magnetic resonance (^1H -NMR) is as follows.

[0256]

20 ^1H -NMR. δ (CDCl_3): 8.66 (d, 1H), 8.45 (d, 1H), 8.04 (m, 4H), 7.95 (d, 1H), 7.81 (m, 3H), 7.69 (m, 2H), 7.59 (t, 1H), 7.53 (t, 1H), 7.33 (m, 5H), 7.18 (t, 1H), 7.07 (t, 2H), 6.51 (td, 1H), 6.38 (m, 2H), 5.78 (dd, 1H)

[0257]

25 In addition, measurement of the thermal decomposition temperature T_d of the obtained $\text{Ir}(\text{Fdpq})_2(\text{acac})$ was performed by a Thermogravimetry/Differential Thermal Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320) to find $T_d = 347^\circ\text{C}$, and thus, it is determined that the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{pic})$ shows favorable heat resistance.

[0258]

30 Further, FIG. 15 shows an absorption spectrum of the obtained $\text{Ir}(\text{Fdpq})_2(\text{pic})$ in

dichloromethane and an emission spectrum (PL) thereof. It is to be noted that the emission spectrum was obtained when light with a wavelength of 468 nm was used as excitation light, where the light with the wavelength of 468 nm was extracted by separating light from a halogen lamp with the use of a slit. In FIG 15, the horizontal axis indicates a wavelength (nm), the left vertical axis indicates absorbance (no unit), and the right vertical axis indicates emission intensity (a.u.). As can be seen from FIG 15, the obtained organometallic complex Ir(Fdpq)₂(pic) has a plurality of absorption peaks. In addition, the emission spectrum shows luminescence with an emission peak at 625 nm, and this luminescence was visible as red luminescence.

[0259]

The absorption peak at the longest wavelength side has a broad peak in the visible region, which is considered to be an absorption spectrum unique to triplet MLCT transition. Namely, it is determined that Ir(Fdpq)₂(pic) is a compound capable of direct photoexcitation to an excited triplet state and intersystem crossing.

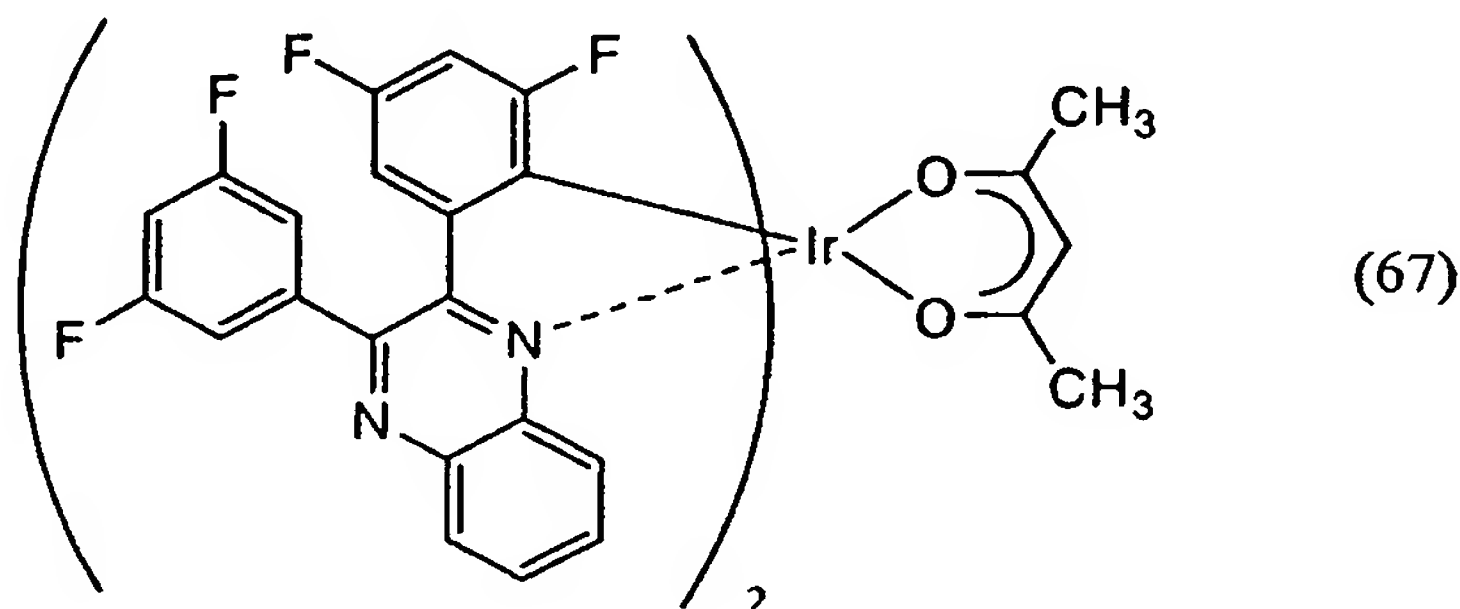
[0260]

(Synthesis Example 4)

In the present synthesis example, synthesis of {2, 3 - bis (3, 5 - difluorophenyl) quinoxalinato} (acetylacetonato) iridium (III) represented by the following formula (67) will be described.

[0261]

The structure formula of Ir(3, 5 - Fdpq)₂(acac) is shown by the following formula (67).



[0262]

<Step 1: Synthesis of 3, 3', 5, 5' - tetrafluorobenzyl>

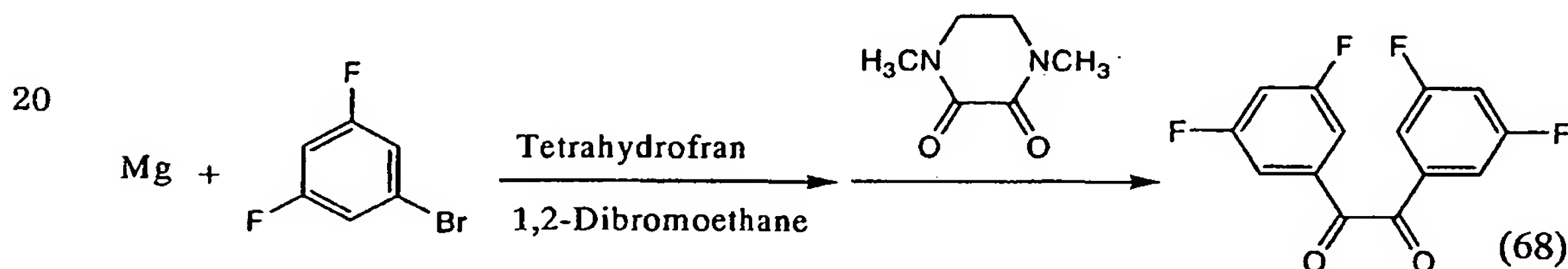
3, 3', 5, 5' - tetrafluorobenzyl that is a material for a ligand was synthesized as follows. First, 3.16 g of magnesium was suspended in 3 mL of tetrahydrofran
 5 (abbreviation: THF), and a small amount of 1, 2 - dibromoethane was added. Into this mixture, a solution of 25.00 g of 1 - bromo - 3, 5 - difluorobenzene in 130 mL of THF was dropped, and stirring was performed for 1.5 hours while holding at reflux on heating. Next, 9.24 g of 1, 4 - dimethylpiperazine - 2, 3 - dione was added to the solution cooled to room temperature, and stirring was performed for 13 hours while
 10 holding at reflux on heating.

[0263]

Further, 200 mL of 10 % hydrochloric acid was added to the solution cooled to room temperature, and the organic layer was extracted with chloroform. After drying with sodium sulfate, the solvent was condensed. Finally, purification was performed
 15 by column chromatography (hexane/dichloromethane system) to obtain 3, 3', 5, 5' - tetrafluorobenzyl (yellow powder, yield: 46 %).

[0264]

The synthesis scheme is shown by the following formula (68).



[0265]

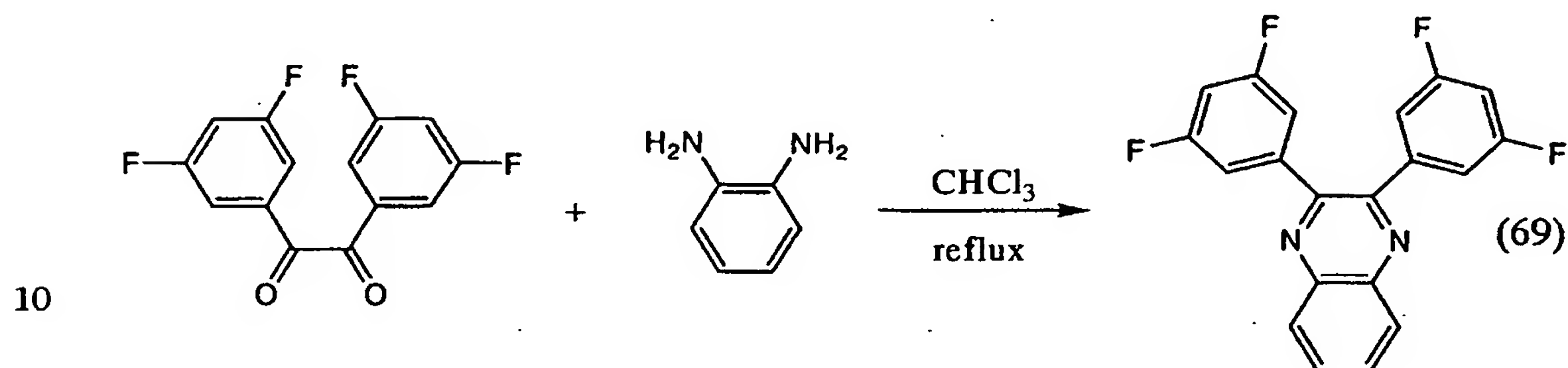
25 <Step 2: Synthesis of ligand H (3, 5 - Fdpq)>

Chloroform (300 mL) was added to 8.32 g of 3, 3', 5, 5' - tetrafluorobenzyl synthesized in Step 1 and 3.19 g of 1, 2 - phenylenediamine, and stirring was performed for 10 hours while holding at reflux on heating. The solution cooled to room temperature was washed with hydrochloric acid (1N) and then a saturated aqueous
 30 solution of sodium chloride, and dried with magnesium sulfate. Then, the solvent was

condensed to obtain 2, 3 - bis (3, 5 - difluorophenyl) quinoxaline (ligand H (3, 5 - Fdpq)) (white powder, yield: 98 %).

[0266]

The synthesis scheme and the structure formula of the ligand H (3, 5 - Fdpq) are shown by the following formula (69).



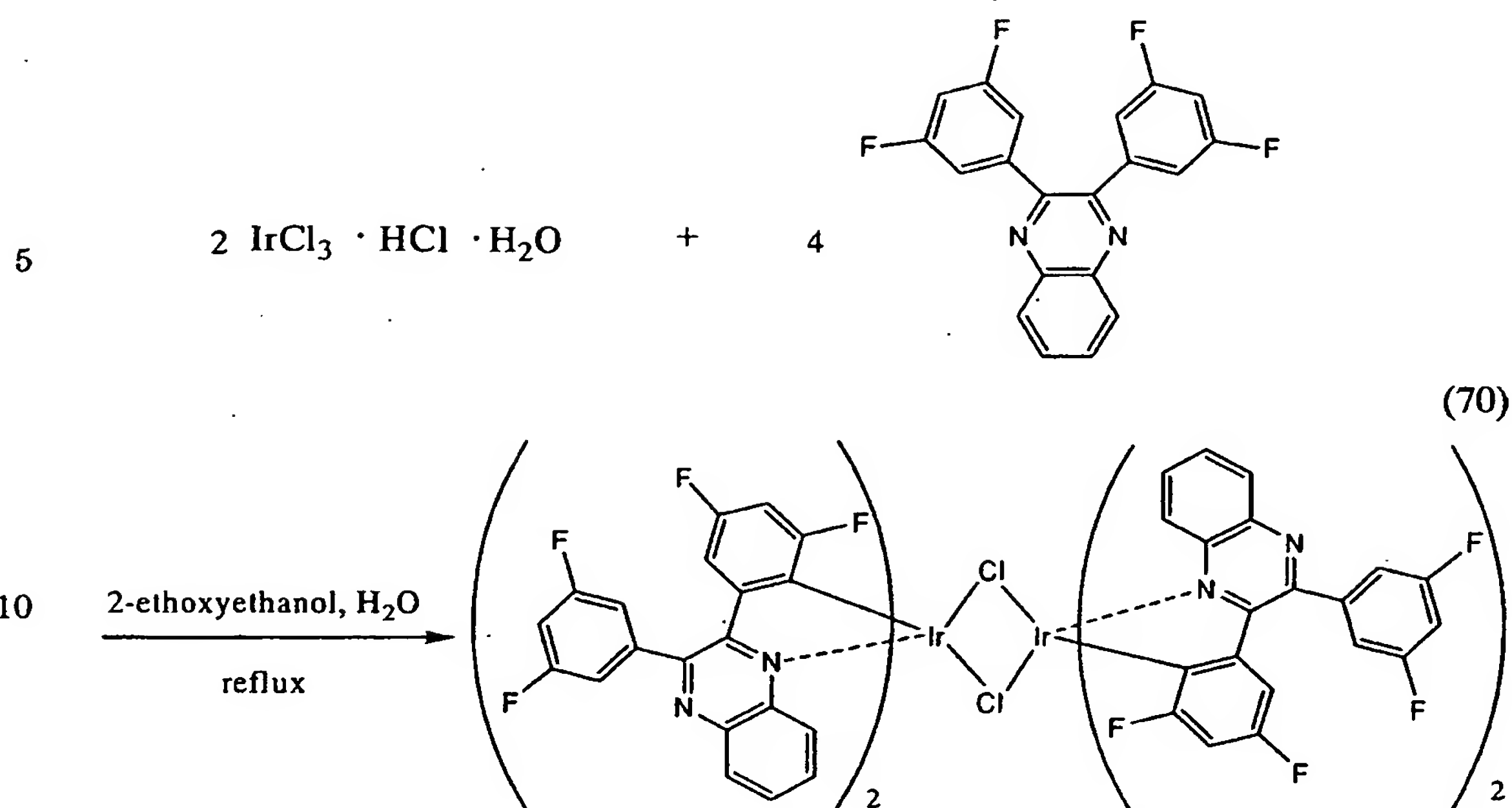
[0267]

<Step 3: Synthesis of Dinuclear Complex $[\text{Ir}(3, 5 - \text{Fdpq})_2\text{Cl}]_2$ >

15 First, with a mixture of 30 mL of 2 - ethoxyethanol and 10 mL of water as a solvent, 2.46 g of the ligand H (3, 5 - Fdpq) synthesized in Step 2 and 0.83 g of iridium chloride ($\text{IrCl}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$) were mixed, and held at reflux in a nitrogen atmosphere for 17 hours to obtain a dinuclear complex $[\text{Ir}(3, 5 - \text{Fdpq})_2\text{Cl}]_2$ (reddish brown powder, yield: 78 %).

[0268]

20 The synthesis scheme and the structure formula of the dinuclear complex $[\text{Ir}(3, 5 - \text{Fdpq})_2\text{Cl}]_2$ are shown by the following formula (70).



[0269]

15 <Step 3: Synthesis of Organometallic Complex $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ >

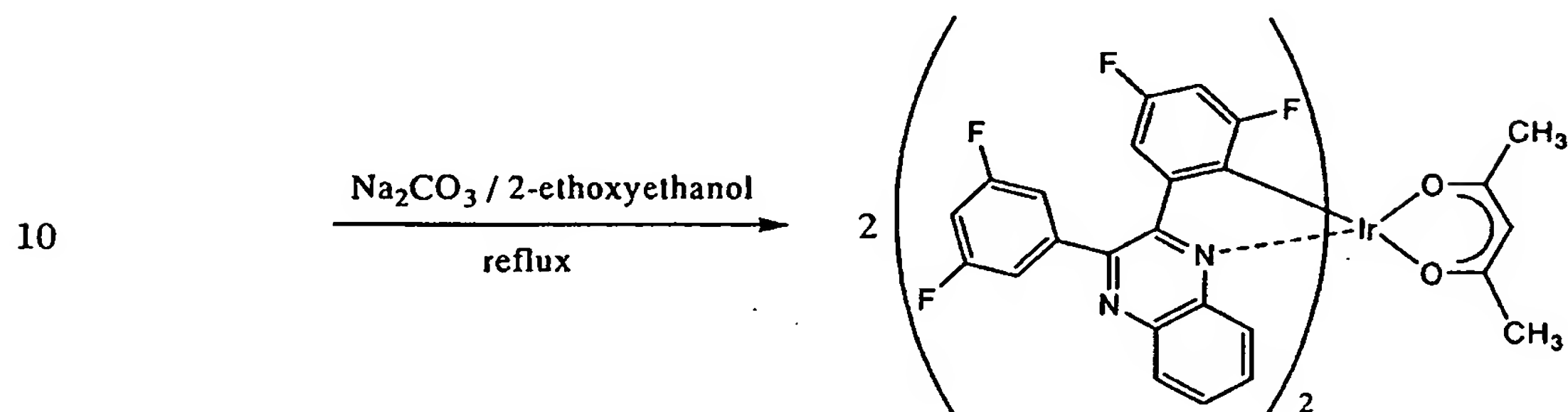
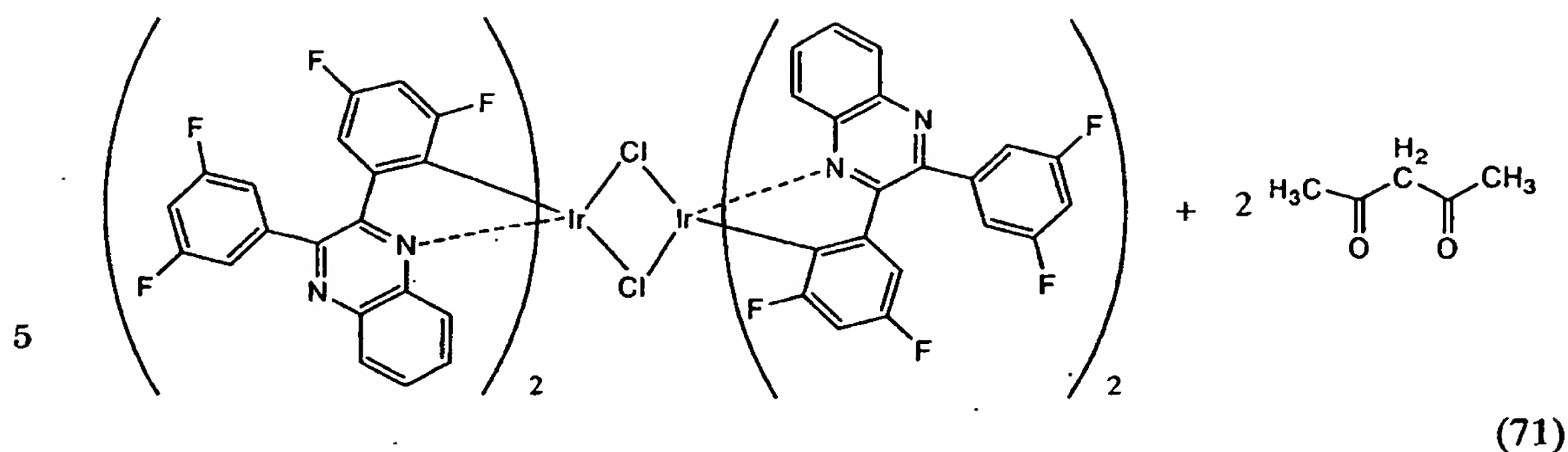
With 30 mL of 2 - ethoxyethanol as a solvent, 2.34 g of the dinuclear complex $[\text{Ir}(3, 5 - \text{Fdpq})_2\text{Cl}]_2$ obtained in Step 3 described above, 0.39 mL of acetylacetone (Hacac), and 1.32 g of sodium carbonate were mixed, and held at reflux in a nitrogen atmosphere for 20 hours to obtain an organometallic complex $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ represented by the formula (67) according to the present invention (dark red powder, yield: 22 %).

[0270]

The synthesis scheme is shown by the following formula (71).

25

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[0271]

The result of analysis of the organometallic complex $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ by nuclear magnetic resonance ($^1\text{H-NMR}$) is as follows.

[0272]

$^1\text{H-NMR}$. δ (CDCl_3): 8.10 (t, 4H), 7.75 (t, 2H), 7.61 (m, 4H), 7.30 (m, 2H), 7.09 (tt, 2H), 6.77 (dd, 2H), 6.20 (td, 2H), 4.67 (s, 1H), 1.61 (s, 6H)

[0273]

In addition, measurement of the thermal decomposition temperature T_d of the obtained $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ was performed by a Thermogravimetry/Differential Thermal Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320) to find $T_d = 342^\circ\text{C}$, and thus, it is determined that the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{pic})$ shows favorable heat resistance.

[0274]

Further, FIG. 16 shows an absorption spectrum of the obtained $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ in dichloromethane and an emission spectrum (PL) thereof. It is to be noted that the emission spectrum was obtained when light with a wavelength of 468 nm was used as excitation light, where the light with the wavelength of 468 nm was extracted by separating light from a halogen lamp with the use of a slit. In FIG. 16, the

horizontal axis indicates a wavelength (nm), the left vertical axis indicates absorbance (no unit), and the right vertical axis indicates emission intensity (a.u.). As can be seen from FIG. 16, the obtained organometallic complex $\text{Ir}(3, 5\text{-Fdpq})_2(\text{acac})$ has a plurality of absorption peaks. In addition, the emission spectrum shows luminescence with an emission peak at 666 nm, and this luminescence was visible as deep red luminescence.

[0275]

The absorption peak at the longest wavelength side has a broad shape in the visible region, which is considered to be an absorption spectrum unique to triplet MLCT transition. Namely, it is determined that $\text{Ir}(3, 5\text{-Fdpq})_2(\text{acac})$ is a compound capable of direct photoexcitation to an excited triplet state and intersystem crossing.

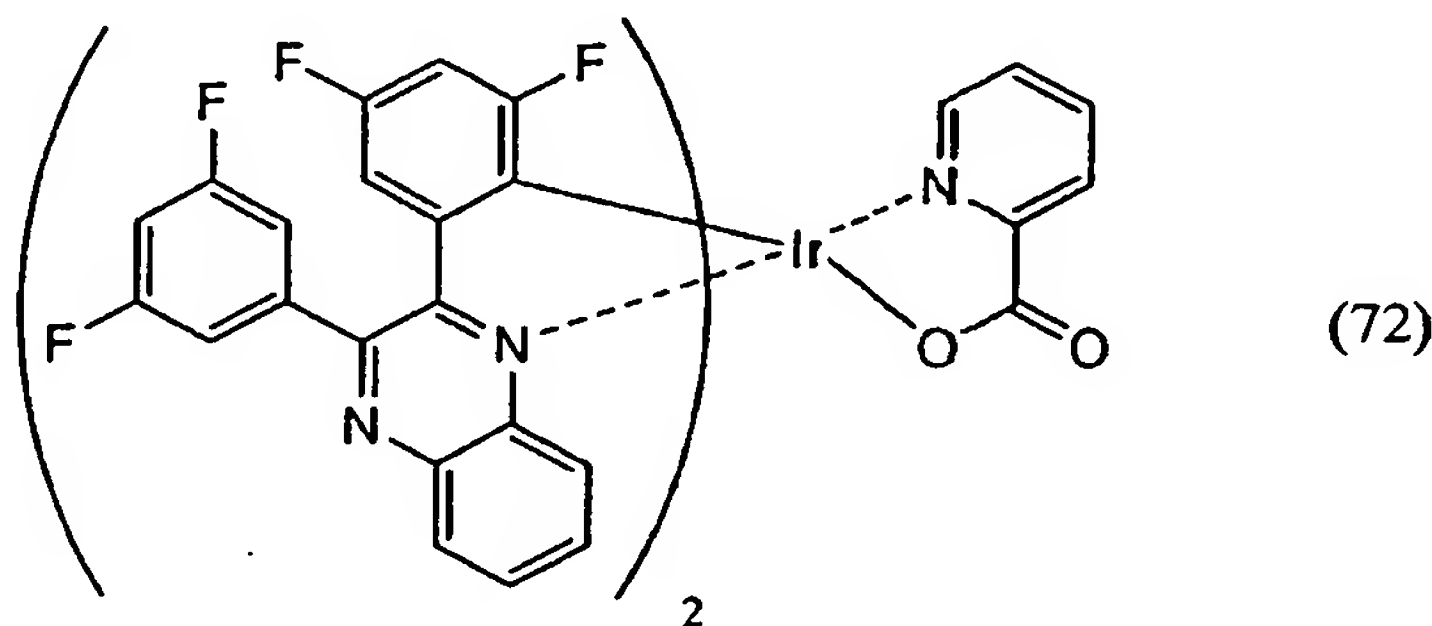
[0276]

(Synthesis Example 5)

In the present synthesis example, synthesis of {2, 3 - bis (3, 5 - difluorophenyl) quinoxalinato} (picolinato) iridium (III) represented by the following formula (72) will be described.

[0277]

The structure formula of $\text{Ir}(3, 5\text{-Fdpq})_2(\text{pic})$ is shown by the following formula (72).



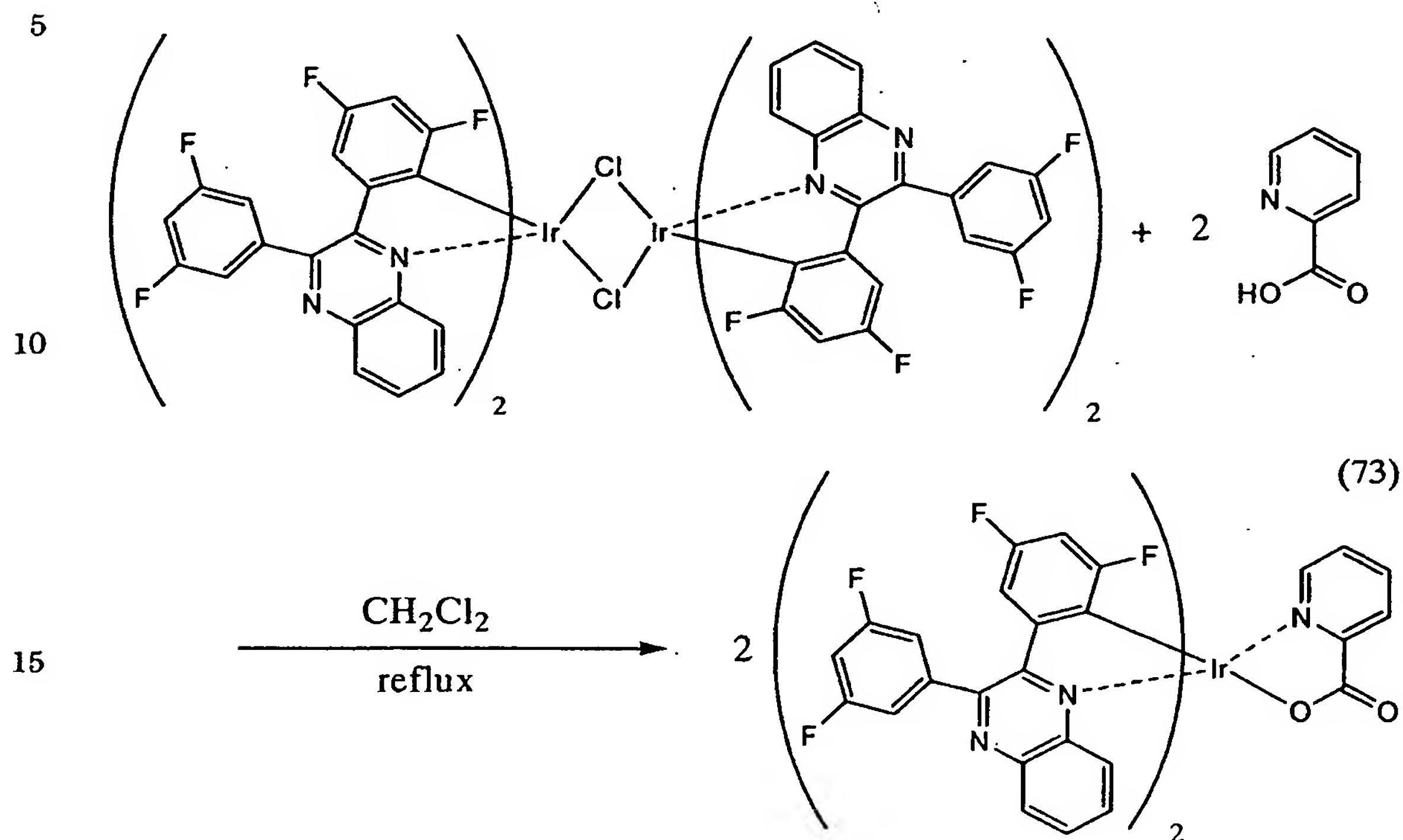
[0278]

With 30 mL of dichloromethane as a solvent, 2.54 g of the dinuclear complex $[\text{Ir}(3, 5\text{-Fdpq})_2\text{Cl}]_2$ synthesized in Step 3 of Synthesis Example 4 and 1.34 g of picolinic acid (Hpic) were mixed, and held at reflux in a nitrogen atmosphere for 16

hours. This solution was filtered to obtain an organometallic complex $\text{Ir}(3, 5\text{-Fdpq})_2(\text{pic})$ according to the present invention (red powder, yield: 14 %).

[0279]

The synthesis scheme is shown by the following formula (73).



[0280]

20 The result of analysis of the organometallic complex $\text{Ir}(3, 5\text{-Fdpq})_2(\text{pic})$ by nuclear magnetic resonance ($^1\text{H-NMR}$) is as follows.

[0281]

$^1\text{H-NMR}$. δ (CDCl_3): 8.65 (d, 1H), 8.54 (d, 1H), 8.06 (m, 2H), 7.87-7.54 (m, 8H), 7.32 (m, 3H), 7.12 (m, 3H), 6.85 (d, 1H), 6.74 (d, 1H), 6.37 (t, 1H), 6.17 (t, 1H)

25

[0282]

In addition, measurement of the thermal decomposition temperature T_d of the obtained $\text{Ir}(3, 5\text{-Fdpq})_2(\text{pic})$ was performed by a Thermogravimetry/Differential Thermal Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320) to find $T_d = 347^\circ\text{C}$, and thus, it is determined that the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{pic})$ shows favorable heat resistance.

30

[0283]

Further, FIG. 17 shows an absorption spectrum of the obtained Ir(3, 5 - Fdpq)₂(pic) in dichloromethane and an emission spectrum (PL) thereof. It is to be noted that the emission spectrum was obtained when light with a wavelength of 468 nm was used as excitation light, where the light with the wavelength of 468 nm was extracted by separating light from a halogen lamp with the use of a slit. In FIG. 17, the horizontal axis indicates a wavelength (nm), the left vertical axis indicates absorbance (no unit), and the right vertical axis indicates emission intensity (a.u.). As can be seen from FIG. 17, the obtained organometallic complex Ir(3, 5 - Fdpq)₂(pic) has a plurality of absorption peaks. In addition, the emission spectrum shows luminescence with an emission peak at 645 nm, and this luminescence was visible as red luminescence.

[0284]

The absorption peak at the longest wavelength side has a broad peak in the visible region, which is considered to be an absorption spectrum unique to triplet MLCT transition. Namely, it is determined that Ir(3, 5 - Fdpq)₂(pic) is a compound capable of direct photoexcitation to an excited triplet state and intersystem crossing.

[0285]

The organometallic complexes described in Synthesis Examples 1 to 5 according to the present invention can be used as a luminescent material or a photosensitizer.

[0286]

Next, from the absorption spectrums of the organometallic complexes according to the present invention, obtained in Synthesis Examples 1 to 5, that is, FIGS. 13 to 17, the energy gap of each organometallic complex was found. The energy gap was calculated by converting the wavelength of the absorption edge of the absorption spectrum to energy. Table 1 shows the results.

[0287] (Table 1)

	abbreviation of organometallic complex according to the present invention	energy gap [eV]
synthesis example 1	Ir(Fdpq) ₂ (acac)	2.0
synthesis example 2	Ir(dpq) ₂ (acac)	1.9
synthesis example 3	Ir(Fdpq) ₂ (pic)	2.0
synthesis example 4	Ir(3, 5-Fdpq) ₂ (acac)	1.9
synthesis example 5	Ir(3, 5-Fdpq) ₂ (pic)	2.0

[0288]

It is to be noted that it is preferable to disperse each of the above-described organometallic complexes according to the present invention appropriately in a host material when the organometallic complex is used as a luminescent material for a light-emitting element. Table 2 shows the energy gaps of typical host materials, measured in the same way as described above.

10

[0289] (Table 2)

abbreviation of typical host material	energy gap [eV]
TPAQn	2.8
CBP	3.5
α -NPD	3.1
Alq ₃	2.8

[0290]

As can be seen from comparison between Table 1 and Table 2, each of the host materials has a larger energy gap than the organometallic complexes according to the present invention, and thus can be used as a host material for the organometallic complexes according to the present invention.

[0291]

Further, in addition to the energy gaps, oxidation and reduction characteristics of the organometallic complexes according to the present invention, obtained in the synthesis examples, were measured by cyclic voltammetry (CV) to evaluate ionization
5 potentials and electron affinities. First, with the use of the organometallic complex $\text{Ir}(\text{Fdpq})_2(\text{acac})$ in Synthesis Example 1 as an example, the procedure of the CV measurement will be described below.

[0292]

As a measurement system, an electrochemical analyzer (ALS Model 600A
10 from BAS) was used. For preparing a solution in the CV measurement, tetra - n - butylammonium perchlorate ($\text{n-Bu}_4\text{NClO}_4$) as a supporting electrolyte was dissolved in dehydrated dimethylformamide (DMF) as a solvent so as to reach a concentration of 100 mmol, and $\text{Ir}(\text{Fdpq})_2(\text{acac})$ as a measuring object was further dissolved to reach a concentration of 1 mmol. In addition, a platinum electrode (PTE platinum electrode
15 from BAS), a platinum electrode (Pt counter electrode for VC-3 from BAS), and a Ag/Ag^+ electrode (RE5 nonaqueous solvent reference electrode from BAS) were used as a work electrode, an auxiliary electrode, and a reference electrode, respectively.

[0293]

The oxidation characteristics were measured by changing the potential of the
20 work electrode with respect to the reference electrode first from -0.4 to 1.2 V, and subsequently from 1.2 to -0.4 V. The reduction characteristics were measured by changing the potential of the work electrode with respect to the reference electrode first from -0.4 to -2.4 V, and subsequently from -2.4 to -0.4 V. It is to be noted that the scan rate in the CV measurement was controlled to be 0.1 V/s.

25 [0294]

FIGS. 18A and 18B show a CV curve showing the oxidation characteristics of $\text{Ir}(\text{Fdpq})_2(\text{acac})$ and a CV curve showing the reduction characteristics of $\text{Ir}(\text{Fdpq})_2(\text{acac})$, respectively. In each of FIGS. 18A and 18B, the horizontal axis and the vertical axis respectively indicate a potential (V) of the work electrode with respect to the reference
30 electrode and a current value (1×10^{-5} A) that flowed between the work electrode and

the auxiliary electrode. From FIG. 18A, it is determined that the oxidation peak potential (E_{ox}) is 0.88 V (vs. Ag/Ag⁺ electrode). In addition, from FIG. 18B, it is determined that the reduction peak potential (E_{re}) is -1.58 V (vs. Ag/Ag⁺ electrode).

[0295]

5 In accordance with the same measurement method, the oxidation peak potential (E_{ox}) and reduction peak potential (E_{re}) were measured also for each of the organometallic complexes according to the present invention, obtained in Synthesis Examples 2 and 3. The results of the CV measurement are arranged in Table 3. It is to be noted that, in the case of these organometallic complexes according to the present
10 invention, there was almost no variation in peak position or peak intensity of the CV curve in each case of oxidation and reduction even when 100 cycles of CV measurement were repeated. Therefore, it is also determined that the organometallic complexes are quite stable against oxidation and reduction reactions.

[0296] (Table 3)

15

	abbreviation of organometallic complex according to the present invention	E_{ox} [eV]	E_{re} [eV]
synthesis example 1	Ir(Fdpq) ₂ (acac)	0.88	-1.58
synthesis example 2	Ir(dpq) ₂ (acac)	0.7 ~ 0.8 *	-1.82
synthesis example 3	Ir(Fdpq) ₂ (pic)	1.0 ~ 1.1 *	-1.51

* The peak is not clear.

[0297]

By the way, when each of the above-described organometallic complexes according to the present invention is used as a luminescent material for a light-emitting
20 element, it is preferable to disperse the organometallic complex appropriately in a host material. Consequently, in accordance with the same measurement method, the oxidation peak potentials and reduction peak potentials of typical host materials were measured. The results are shown in following Table 4.

[0298] (Table 4)

abbreviation of typical host material	E_{ox} [eV]	E_{re} [eV]
TPAQn	0.69	-2.05
CBP ^{*1}	1.25	-2.3 ~ -2.4 ^{*2}
α -NPD	0.45	-2.8 ~ -2.9 ^{*2}
Alq ₃	0.7 ~ 0.8 ^{*2}	-2.20

*1 Dichloromethane is used as solvent.

*2 The peak is not clear.

5 [0299]

When Table 4 is compared with Table 3, it is first determined that each organometallic complex according to the present invention especially has a larger reduction potential than the host materials (the reduction potential has a smaller absolute value). This namely indicates that the organometallic complex according to the present invention has a larger electron affinity than the host materials (is more easily reduced), and accordingly suggests that the organometallic complex according to the present invention has a property of easily receiving electrons and carriers can be efficiently trapped by dispersing the organometallic complex in the host material described above.

15 [0300]

In addition, depending on the combination, the organometallic complex according to the present invention has a smaller oxidation potential than the host material (for example, a combination of Ir(Fdpq)₂(acac) and Alq₃, and a case of using CBP as the host material). In the case of such a combination, the organometallic complex according to the present invention has a smaller ionization potential than the host materials (is more easily oxidized). Accordingly, when such a combination is applied to a light-emitting element, it is possible to trap not only electrons but also holes efficiently.

[0301]

As a host material, it is preferable to use a material that allows the organometallic complex according to the present invention to trap electrons and holes efficiently. However, it is not necessary to trap both an electron and a hole, and either one may be trapped. In addition, when the energy gap of a host material is larger than
5 the energy gap of the organometallic complex, it is not always necessary to use a material that allows the organometallic complex according to the present invention to trap electrons and holes efficiently.

[0302]

10 [Embodiment 2]

In the present embodiment, the structure of a light-emitting element according to the present invention and a manufacturing method thereof will be described with reference to FIG. 19.

[0303]

15 First, on a substrate 1300, a first electrode 1301 was formed by deposition of indium tin oxide so as to be 110 nm in film thickness. It is to be noted that sputtering was used for the deposition.

[0304]

20 Next, on the first electrode 1301, a hole injecting layer 1311 was formed by deposition of copper phthalocyanine so as to be 20 nm in film thickness. The deposition was performed by evaporation using resistance heating in such a way that the substrate on which the first electrode 1301 was formed was fixed in a substrate holder of a commercially produced vacuum deposition system with the surface at which the first electrode 1301 was formed down and copper phthalocyanine was put in an
25 evaporation source provided in the vacuum deposition system.

[0305]

30 Next, on the hole injecting layer 1311, a hole transporting layer 1312 was formed by deposition of α -NPD so as to be 40 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer 1311.

[0306]

Next, a light-emitting layer 1313 was formed by deposition of α -NPD so that {2, 3 - bis (4 - fluorophenyl) quinoxalinato} (acetylacetonato) iridium (III) (hereinafter, referred to as Ir(Fdpq)₂(acac)) represented by the formula (16) is included at a rate of 8 weight% in α -NPD. The deposition was performed by co-evaporation with α -NPD and Ir(Fdpq)₂(acac) as evaporation sources so as to be 30 nm in film thickness. Here, α -NPD functions as a host material.

[0307]

Next, on the light-emitting layer 1313, an electron transporting layer 1314 was formed by deposition of Alq₃ so as to be 30 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer 1311. Then, on the electron transporting layer 1314, an electron injecting layer 1315 was formed by deposition of calcium fluoride (CaF₂) so as to be 1 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer 1311.

[0308]

In this way, a layer including a luminescent material 1302 was formed by stacking the hole injecting layer 1311, the hole transporting layer 1312, the light-emitting layer 1313, the electron transporting layer 1314, and the electron injecting layer 1315.

[0309]

Next, on the electron injecting layer 1315, a second electrode 1303 was formed by deposition of aluminum so as to be 150 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer 1311.

[0310]

Further, the manufactured light-emitting element was moved into a glove box in a nitrogen atmosphere, and sealing was performed with the use of a sealing material in the glove box. After sealing of the light-emitting element, the light-emitting element was taken outside the glove box, and current density-luminance characteristics,

voltage-luminance characteristics, and luminance-current efficiency characteristics in an initial condition were examined at room temperature (about 25°C). In addition, an operational stability test by constant current driving was performed to examine the lifetime of the element.

5 [0311]

First, FIGS. 20A to 20C show initial characteristics of the manufactured light-emitting element. FIG. 20A shows current density-luminance characteristics, FIG. 20B shows voltage-luminance characteristics, and FIG. 20C shows luminance-current efficiency characteristics. From the voltage-luminance characteristics, it is determined
10 that light was emitted with a luminance of 440 cd/m² when a voltage of 9.0 V was applied, and that the luminous efficiency was 1.0 cd/A in that case. Further, the emission spectrum has a peak at a wavelength of 647 nm, and the element exhibits CIE chromaticity coordinates of (x, y) = (0.67, 0.32), from which it is determined that red or reddish luminescence with quite high color purity is provided due to Ir(Fdpq)₂(acac).

15 [0312]

Next, the operational stability test was performed by constant current driving in which a current with a constant current value is applied for a certain period of time. As a test method, a current of a current density (44.3 mA/cm²) required for emitting light with a luminance of 440 cd/m² in the initial condition was kept applied for a
20 certain period of time to examine change in luminance with time. In the result, the luminance after a lapse of 3800 hours was kept at 68 % of the luminance in the initial condition without reducing by half. From this result, it is determined that the light-emitting element according to the present invention is small reduced in luminance with time, and has a favorable lifetime.

25 [0313]

Further, this operational stability test was performed ongoingly. FIG. 21 shows the obtained test result, where the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). Based on the result shown in FIG. 21, the half life of
30 the luminance was estimated by an extrapolation method to approximate 8000 hours.

[0314]

[Embodiment 3]

In the present embodiment, the structure of a light-emitting element using Alq_3 as a host material according to the present invention and a manufacturing method thereof will be described with reference to FIG. 22.

[0315]

First, on a substrate 1400, a first electrode 1401 was formed by deposition of indium tin oxide so as to be 110 nm in film thickness. It is to be noted that sputtering was used for the deposition.

[0316]

Next, on the first electrode 1401, a hole injecting layer 1411 was formed by deposition of DNTPD so as to be 20 nm in film thickness. The deposition was performed by evaporation using resistance heating in such a way that the substrate on which the first electrode 1401 was formed was fixed in a substrate holder of a commercially produced vacuum deposition system with the surface at which the first electrode 1401 was formed down and DNTPD was put in an evaporation source provided in the vacuum deposition system.

[0317]

Next, on the hole injecting layer 1411, a hole transporting layer 1412 was formed by deposition of α -NPD so as to be 10 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer 1411.

[0318]

Next, a light-emitting layer 1413 was formed by deposition of Alq_3 so that {2, 3 - bis (4 - fluorophenyl) quinoxalinato} (acetylacetonato) iridium (III) (hereinafter, referred to as $\text{Ir}(\text{Fdpq})_2(\text{acac})$) represented by the formula (16) is included at a rate of 8 weight% in Alq_3 . The deposition was performed by co-evaporation with Alq_3 and $\text{Ir}(\text{Fdpq})_2(\text{acac})$ as evaporation sources so as to be 30 nm in film thickness. Here, Alq_3 functions as a host material.

[0319]

Next, on the light-emitting layer 1413, an electron transporting layer 1414 was formed by deposition of Alq_3 so as to be 30 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer
5 1411.

[0320]

Next, on the electron transporting layer 1414, an electron injecting layer 1415 was formed by deposition of calcium fluoride (CaF_2) so as to be 1 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the
10 hole injecting layer 1411.

[0321]

In this way, a layer including a luminescent material 1402 was formed by stacking the hole injecting layer 1411, the hole transporting layer 1412, the light-emitting layer 1413, the electron transporting layer 1414, and the electron injecting
15 layer 1415.

[0322]

Next, on the electron injecting layer 1415, a second electrode 1403 was formed by deposition of aluminum so as to be 150 nm in film thickness. The deposition was performed by evaporation in the same way as the formation of the hole injecting layer
20 1411.

[0323]

Further, the manufactured light-emitting element was moved into a glove box in a nitrogen atmosphere, and sealing was performed with the use of a sealing material in the glove box. After sealing of the light-emitting element, the light-emitting
25 element was taken outside the glove box, and current density-luminance characteristics, voltage-luminance characteristics, and luminance-current efficiency characteristics in an initial condition were examined at room temperature (about 25°C). In addition, an operational stability test by constant current driving was performed to examine the lifetime of the element.

30 [0324]

First, FIGS. 23A to 23C show initial characteristics of the manufactured light-emitting element. FIG. 23A shows current density-luminance characteristics, FIG. 23B shows voltage-luminance characteristics, and FIG. 23C shows luminance-current efficiency characteristics. From the voltage-luminance characteristics, it is determined that light was emitted with a luminance of 470 cd/m^2 when a voltage of 10.6 V was applied, and that the luminous efficiency was 1.1 cd/A in that case. Further, the emission spectrum has a peak at a wavelength of 659 nm, and the element exhibits CIE chromaticity coordinates of $(x, y) = (0.70, 0.30)$, from which it is determined that red or reddish luminescence with quite high color purity is provided due to $\text{Ir}(\text{Fdpq})_2(\text{acac})$.

10 [0325]

Next, the operational stability test by constant current driving was performed. As a test method, a current of a current density (41.7 mA/cm^2) required for emitting light with a luminance of 470 cd/m^2 in the initial condition was kept applied for a certain period of time to examine change in luminance with time. In the result, the luminance after a lapse of 1400 hours was kept at 89 % of the luminance in the initial condition without reducing by half. From this result, it is determined that the light-emitting element according to the present invention is small reduced in luminance with time, and has a favorable lifetime.

15 [0326]

Further, this operational stability test was performed ongoingly. FIG. 24 shows the obtained test result, where the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). Based on the result shown in FIG. 24, the half life of the luminance was estimated by an extrapolation method to approximate 34000 hours.

25

[0327]

[Embodiment 4]

In the present embodiment, an example of a light-emitting element using two kinds of materials, α -NPD and Alq_3 , as host materials will be described. The element in the present embodiment was manufactured in the same way as in Embodiment 3

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except the structure of a light-emitting layer 1413 as described below.

[0328]

The light-emitting layer 1413 was formed by three-source evaporation in which Ir(Fdpq)₂(acac) represented by the formula (16) was evaporated while setting the evaporation rate of α -NPD at 0.4 nm/s and setting the evaporation rate of Alq₃ at 0.1 nm/s. In this case, the addition amount of Ir(Fdpq)₂(acac) was controlled so as to be 8 weight% with respect to α -NPD. In addition, the film thickness of the light-emitting layer 1413 was made to be 30 nm. Here, α -NPD and Alq₃ function as host materials.

[0329]

Further, the manufactured light-emitting element was moved into a glove box in a nitrogen atmosphere, and sealing was performed with the use of a sealing material in the glove box. After sealing of the light-emitting element, the light-emitting element was taken outside the glove box, and current density-luminance characteristics, voltage-luminance characteristics, and luminance-current efficiency characteristics in an initial condition were examined at room temperature (about 25°C). In addition, an operational stability test by constant current driving was performed to examine the lifetime of the element.

[0330]

First, FIGS. 25A to 25C show initial characteristics of the manufactured light-emitting element. FIG. 25A shows current density-luminance characteristics, FIG. 25B shows voltage-luminance characteristics, and FIG. 25C shows luminance-current efficiency characteristics. From the result, it is determined that light was emitted with a luminance of 510 cd/m² when a voltage of 7.6 V was applied, and that the luminous efficiency was 1.3 cd/A in that case. Further, the emission spectrum has a peak at a wavelength of 640 nm, and the element exhibits CIE chromaticity coordinates of (x, y) = (0.70, 0.30), from which it is determined that red or reddish luminescence with quite high color purity is provided due to Ir(Fdpq)₂(acac).

[0331]

Next, the operational stability test by constant current driving was performed. As a test method, a current of a current density (37.8 mA/cm²) required for emitting

light with a luminance of 510 cd/m^2 in the initial condition was kept applied for a certain period of time to examine change in luminance with time. In the result, the luminance after a lapse of 1200 hours was kept at 90 % of the luminance in the initial condition without reducing by half. From this result, it is determined that the
5 light-emitting element according to the present invention is small reduced in luminance with time, and has a favorable lifetime.

[0332]

Further, this operational stability test was performed ongoingly. FIG. 26 shows the obtained test result, where the horizontal axis indicates time (h), and the
10 vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). Based on the result shown in FIG. 26, the half life of the luminance was estimated by an extrapolation method to approximate 40000 hours.

[0333]

15 [Embodiment 5]

In the present embodiment, the structure of a light-emitting element using an organometallic complex according to the present invention as a luminescent material and a manufacturing method thereof will be described with reference to FIG. 19. The present embodiment is an example in which a light-emitting layer has the same structure
20 as that in Embodiment 2, and the thickness and material of the other layer are optimized to further improve the luminous efficiency.

[0334]

On a substrate 1300, indium tin oxide including silicon oxide was deposited by sputtering to form a first electrode 1301. The film thickness thereof was made to be
25 110 nm.

[0335]

Next, the substrate 1300 on which the first electrode 1301 was formed was fixed in a substrate holder provided in a vacuum deposition system so that the surface at which the first electrode 1301 was formed was made down.

30 [0336]

Next, on the first electrode 1301, 4, 4' - bis [N - {4 - (N, N - di - m - tolylamino) phenyl} - N - phenylamino] biphenyl (abbreviation: DNTPD) was deposited by evaporation using resistance heating so as to be 50 nm in film thickness to form a hole injecting layer 1311.

5 [0337]

Next, on the hole injecting layer 1311, α -NPD was deposited by evaporation using resistance heating so as to be 10 nm in film thickness to form a hole transporting layer 1312.

[0338]

10 Next, on the hole transporting layer 1312, $\text{Ir}(\text{Fdpq})_2(\text{acac})$ and α -NPD were deposited by co-evaporation so as to be 30 nm in film thickness to form a light-emitting layer 1313. Here, the mass ratio of $\text{Ir}(\text{Fdpq})_2(\text{acac})$ to α -NPD was made to be 1 : 0.08 (= α -NPD : $\text{Ir}(\text{Fdpq})_2(\text{acac})$). This ratio makes $\text{Ir}(\text{Fdpq})_2(\text{acac})$ dispersed in a layer composed of α -NPD. It is to be noted that co-evaporation is an evaporation method in
15 which evaporation is performed simultaneously from a plurality of evaporation sources in one processing room.

[0339]

Next, on the light-emitting layer 1313, Alq_3 was deposited by evaporation using resistance heating so as to be 70 nm in film thickness to form an electron
20 transporting layer 1314.

[0340]

Next, on the electron transporting layer 1314, calcium fluoride was deposited by evaporation using resistance heating so as to be 1 nm in film thickness to form an electron injecting layer 1315.

25 [0341]

Next, on the electron injecting layer 1315, aluminum was deposited by evaporation using resistance heating so as to be 200 nm in film thickness to form a second electrode 1303.

[0342]

30 Sealing of the thus manufactured light-emitting element was performed in a

nitrogen atmosphere. After that, in order to examine operation characteristics, a voltage was applied so that the potential of the first electrode 1301 was higher than the potential of the second electrode 1303. It is to be noted that the measurement was performed while maintaining at room temperature (25°C). FIGS. 27A to 27C show results of this measurement. FIG. 27A shows a result of examining current density-luminance characteristics, FIG. 27B shows a result of examining voltage-luminance characteristics, and FIG. 27C shows a result of examining luminance-current efficiency characteristics. In FIG. 27A, the horizontal axis and the vertical axis respectively indicate a current density (mA/cm²) and luminance (cd/m²). In FIG. 27B, the horizontal axis and the vertical axis respectively indicate a voltage (V) and luminance (cd/m²). In FIG. 27C, the horizontal axis and the vertical axis respectively indicate luminance (cd/m²) and a current efficiency (cd/A).

[0343]

From these results, it is determined that light was emitted with a luminance of 520 cd/m² when a voltage of 7.2 V was applied. The current efficiency in this case was 3.8 cd/A. Further, the emission spectrum has a peak at a wavelength of 644 nm, and the element exhibits CIE chromaticity coordinates of (x, y) = (0.66, 0.33), from which it is determined that red or reddish luminescence with quite high color purity is provided due to Ir(Fdpq)₂(acac).

[0344]

Next, change in luminance with time was examined by an operational stability test. The operational stability test was performed in such a way that a current of a current density (13.9 mA/cm² in the case of the light-emitting element in the present embodiment) required for emitting light with a luminance of 520 cd/m² in the initial condition was kept applied for a certain period of time and the luminance was measured at each elapsed time. It is to be noted that the test was performed while maintaining at room temperature (25°C).

[0345]

FIG. 28 shows the result of the operational stability test. In FIG. 28, the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance

to the luminance in the initial condition (that is, relative luminance (%)). From FIG 28, it is determined that the relative luminance after a lapse of 1400 hours was 95 %, that is, the initial luminance was degraded by 5 %, without reaching half the initial luminance. Namely, it is determined that the light-emitting element according to the present invention is an element that has a favorable lifetime. In addition, based on the result shown in FIG 28, the half life of the luminance was estimated by an extrapolation method to approximate 19000 hours.

[0346]

10 [Embodiment 6]

[0347]

In the present embodiment, the structure of a light-emitting layer using an organometallic complex according to the present invention as a luminescent material and a manufacturing method thereof will be described with reference to FIG. 22. Embodiment 6 is an example in which a light-emitting element has the same structure as that in Embodiment 3, and the thickness and material of the other layer are optimized to further improve the luminous efficiency.

[0348]

On a substrate 1400, indium tin oxide including silicon oxide was deposited by sputtering to form a first electrode 1401. The film thickness thereof was made to be 110 nm.

[0349]

Next, the substrate 1400 on which the first electrode 1401 was formed was fixed in a substrate holder provided in a vacuum deposition system so that the surface at which the first electrode 1401 was formed was made down.

[0350] Next, on the first electrode 1401, DNTPD was deposited by evaporation using resistance heating so as to be 50 nm in film thickness to form a hole injecting layer 1411.

[0351]

Next, on the hole injecting layer 1411, α -NPD was deposited by evaporation

using resistance heating so as to be 10 nm in film thickness to form a hole transporting layer 1412.

[0352]

Next, on the hole transporting layer 1412, $\text{Ir}(\text{Fdpq})_2(\text{acac})$ and Alq_3 were deposited by co-evaporation so as to be 30 nm in film thickness to form a light-emitting layer 1413. Here, the mass ratio of $\text{Ir}(\text{Fdpq})_2(\text{acac})$ to Alq_3 was made to be 1 : 0.08 (= Alq_3 : $\text{Ir}(\text{Fdpq})_2(\text{acac})$). This ratio makes $\text{Ir}(\text{Fdpq})_2(\text{acac})$ dispersed in a layer composed of Alq_3 . It is to be noted that co-evaporation is an evaporation method in which evaporation is performed simultaneously from a plurality of evaporation sources in one processing room.

[0353]

Next, on the light-emitting layer 1413, Alq_3 was deposited by evaporation using resistance heating so as to be 70 nm in film thickness to form an electron transporting layer 1414.

15 [0354]

Next, on the electron transporting layer 1414, calcium fluoride was deposited by evaporation using resistance heating so as to be 1 nm in film thickness to form an electron injecting layer 1415.

[0355]

20 Next, on the electron injecting layer 1415, aluminum was deposited by evaporation using resistance heating so as to be 200 nm in film thickness to form a second electrode 1403.

[0356]

Sealing of the thus manufactured light-emitting element was performed in a nitrogen atmosphere. After that, in order to examine operation characteristics, a voltage was applied so that the potential of the first electrode 1401 was higher than the potential of the second electrode 1403. It is to be noted that the measurement was performed while maintaining at room temperature (25°C). FIGS. 29A to 29C show results of this measurement. FIG. 29A shows a result of examining current density-luminance characteristics, FIG. 29B shows a result of examining

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voltage-luminance characteristics, and FIG. 29C shows a result of examining luminance-current efficiency characteristics. In FIG. 29A, the horizontal axis and the vertical axis respectively indicate a current density (mA/cm^2) and luminance (cd/m^2). In FIG. 29B, the horizontal axis and the vertical axis respectively indicate a voltage (V) and luminance (cd/m^2). In FIG. 29C, the horizontal axis and the vertical axis respectively indicate luminance (cd/m^2) and a current efficiency (cd/A).

[0357]

From these results, it is determined that light was emitted with a luminance of $490 \text{ cd}/\text{m}^2$ when a voltage of 8.6 V was applied. The luminous efficiency in this case was $3.7 \text{ cd}/\text{A}$. Further, the emission spectrum has a peak at a wavelength of 656 nm, and the element CIE chromaticity coordinates of $(x, y) = (0.64, 0.34)$, from which it is determined that red or reddish luminescence with quite high color purity is provided due to $\text{Ir}(\text{Fdpq})_2(\text{acac})$.

[0358]

Next, change in luminance with time was examined by an operational stability test. The operational stability test was performed in such a way that a current of a current density ($13.3 \text{ mA}/\text{cm}^2$ in the case of the light-emitting element in the present embodiment) required for emitting light with a luminance of $490 \text{ cd}/\text{m}^2$ in the initial condition was kept applied for a certain period of time and the luminance was measured at each elapsed time. It is to be noted that the test was performed while maintaining at room temperature (25°C).

[0359]

FIG. 30 shows the result of the operational stability test. In FIG. 30, the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). From FIG. 30, it is determined that the relative luminance after a lapse of 1800 hours was 84 %, that is, the initial luminance was degraded by 16 %, without reaching half the initial luminance. Namely, it is determined that the light-emitting element according to the present invention is an element that has a favorable lifetime. In addition, based on the result shown in FIG. 30, the half life of the luminance was estimated by an extrapolation

method to approximate 33000 hours.

[0360]

[Embodiment 7]

5 The present embodiment is an example of a light-emitting element manufactured in the same way as in Embodiment 6 except changing the structures of the electron transporting layer 1414 and the electron injecting layer 1415 as described below, and will be described with reference to FIG. 22.

[0361]

10 In the present embodiment, the film thickness of the electron transporting layer 1414 was made to be 30 nm. In addition, the electron injecting layer 1415 was formed by co-evaporation of Alq₃ and Li so as to be 40 nm in film thickness. Here, the mass ratio of Li to Alq₃ was made to be 1 : 0.01 (=Alq₃ : Li).

[0362]

15 Sealing of the thus manufactured light-emitting element was performed in a nitrogen atmosphere. After that, in order to examine operation characteristics, a voltage was applied so that the potential of the first electrode 1401 was higher than the potential of the second electrode 1403. It is to be noted that the measurement was performed while maintaining at room temperature (25°C). FIGS. 31A to 31C show
20 results of this measurement. FIG. 31A shows a result of examining current density-luminance characteristics, FIG. 31B shows a result of examining voltage-luminance characteristics, and FIG. 31C shows a result of examining luminance-current efficiency characteristics. In FIG. 31A, the horizontal axis and the vertical axis respectively indicate a current density (mA/cm²) and luminance (cd/m²).
25 In FIG. 31B, the horizontal axis and the vertical axis respectively indicate a voltage (V) and luminance (cd/m²). In FIG. 31C, the horizontal axis and the vertical axis respectively indicate luminance (cd/m²) and a current efficiency (cd/A).

[0363]

From these results, it is determined that light was emitted with a luminance of
30 480 cd/m² when a voltage of 7.6 V was applied. The current efficiency in this case

was 3.5 cd/A. Further, the emission spectrum has a peak at a wavelength of 656 nm, and the element exhibits CIE chromaticity coordinates of $(x, y) = (0.66, 0.33)$, from which it is determined that red or reddish luminescence with quite high color purity is provided due to $\text{Ir}(\text{Fdpq})_2(\text{acac})$.

5 [0364]

Next, change in luminance with time was examined by an operational stability test. The operational stability test was performed in such a way that a current of a current density (13.7 mA/cm^2 in the case of the light-emitting element in the present embodiment) required for emitting light with a luminance of 480 cd/m^2 in the initial condition was kept applied for a certain period of time and the luminance was measured at each elapsed time. It is to be noted that the test was performed while maintaining at room temperature (25°C). FIG. 32 shows the result of the operational stability test. In FIG. 32, the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). From FIG. 32, it is determined that the relative luminance after a lapse of 740 hours was 86 %, that is, the initial luminance was degraded by 14 %, without reaching half the initial luminance. Namely, it is determined that the light-emitting element according to the present invention is an element that has a favorable lifetime. In addition, based on the result shown in FIG. 32, the half life of the luminance was estimated by an extrapolation method to approximate 36000 hours.

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15
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[0365]

[Embodiment 8]

Embodiment 8 is an example in which a light-emitting layer has the same structure as that in Embodiment 4, and the thickness and material of the other layer are optimized to further improve the luminous efficiency, and an example of a light-emitting element manufactured in the same way as in Embodiment 6 except changing the structures of the electron transporting layer 1414 and the electron injecting layer 1415 as described below. A description will be given with reference to FIG. 22.

25

30 [0366]

In the present embodiment, the light-emitting layer 1413 was formed by three-source evaporation in which α -NPD, Alq₃, and Ir(Fdpq)₂(acac) were evaporated simultaneously. In this case, the deposition ratio was set so that the mass ratio is Alq₃ : α -NPD : Ir(Fdpq)₂(acac) = 1 : 1 : 0.08. In addition, the film thickness of the light-emitting layer 1413 was made to be 30 nm. Here, α -NPD and Alq₃ function as host materials. In addition, the film thickness of the electron transporting layer 1414 was made to be 60 nm.

[0367]

Sealing of the thus manufactured light-emitting element was performed in a nitrogen atmosphere. After that, in order to examine operation characteristics, a voltage was applied so that the potential of the first electrode 1401 was higher than the potential of the second electrode 1403. It is to be noted that the measurement was performed while maintaining at room temperature (25°C). FIGS. 33A to 33C show results of this measurement. FIG. 33A shows a result of examining current density-luminance characteristics, FIG. 33B shows a result of examining voltage-luminance characteristics, and FIG. 33C shows a result of examining luminance-current efficiency characteristics. In FIG. 33A, the horizontal axis and the vertical axis respectively indicate a current density (mA/cm²) and luminance (cd/m²). In FIG. 33B, the horizontal axis and the vertical axis respectively indicate a voltage (V) and luminance (cd/m²). In FIG. 33C, the horizontal axis and the vertical axis respectively indicate luminance (cd/m²) and a current efficiency (cd/A).

[0368]

From these results, it is determined that light was emitted with a luminance of 560 cd/m² when a voltage of 7.8 V was applied. The luminous efficiency in this case was 3.6 cd/A. Further, the emission spectrum has a peak at a wavelength of 651 nm, and the element exhibits CIE chromaticity coordinates of (x, y) = (0.68, 0.31), from which it is determined that red or reddish luminescence with quite high color purity is provided due to Ir(Fdpq)₂(acac).

[0369]

Next, change in luminance with time was examined by an operational stability

test. The operational stability test was performed in such a way that a current of a current density (15.6 mA/cm^2 in the case of the light-emitting element in the present embodiment) required for emitting light with a luminance of 560 cd/m^2 in the initial condition was kept applied for a certain period of time and the luminance was measured at each elapsed time. It is to be noted that the test was performed while maintaining at room temperature (25°C).

[0370]

FIG. 34 shows the result of the operational stability test. In FIG. 34, the horizontal axis indicates time (h), and the vertical axis indicates the ratio of a luminance to the luminance in the initial condition (that is, relative luminance (%)). From FIG. 34, it is determined that the relative luminance after a lapse of 640 hours was 84 %, that is, the initial luminance was degraded by 16 %, without reaching half the initial luminance. Namely, it is determined that the light-emitting element according to the present invention is an element that has a favorable lifetime. In addition, based on the result shown in FIG. 34, the half life of the luminance was estimated by an extrapolation method to approximate 68000 hours.

[0371]

[Embodiment 9]

In the present embodiment, a light-emitting device that has a light-emitting element according to the present invention in a pixel portion will be described with reference to FIG. 35A and 35B. FIG. 35A is a top view showing the light-emitting device and FIG. 35B is a cross-sectional view taken along line A-A' in FIG. 35A. Reference numeral 1501 indicated by a dotted line denotes a driver circuit portion (a source side driver circuit), reference numeral 1502 denotes a pixel portion, and reference numeral 1503 denotes a driver circuit portion (a gate side driver circuit). In addition, reference numerals 1504 and 1505 denote a sealing substrate and a sealing material, respectively. The inside 1506 surrounded by the sealing material 1505 is a space.

[0372]

Further, reference numeral 1507 denotes a wiring for transmitting signals to be input to the source side driver circuit 1501 and the gate side driver circuit 1503, and receives signals such as a video signal, a clock signal, a start signal, and a reset signal from an FPC (Flexible Printed Circuit) 1508 that serves as an external input terminal.

5 It is to be noted that although only the FPC is shown in the FIGure here, a printed wiring board (PWB) may be attached to this FPC. The light-emitting device according to the present invention includes not only a light-emitting device body but also a state in which an FPC or a PWB is attached thereto.

[0373]

10 Next, the sectional structure will be explained with reference to FIG. 35B. Although the driver circuits and the pixel portion are formed over a substrate 1509, the source side driver circuit 1501 as the driver circuit portion and the pixel portion 1502 are shown here.

[0374]

15 In the source side driver circuit 1501, a CMOS circuit is formed by a combination of an n-channel TFT 1517 and a p-channel TFT 1518. The TFTs forming the driver circuit may be formed by a known CMOS circuit, PMOS circuit, or NMOS circuit. Although the present embodiment shows a driver integrated type in which a driver circuit is formed over a substrate, which is not always necessary, the driver circuit
20 can be formed not over the substrate but outside the substrate.

[0375]

The pixel portion 1502 has a plurality of pixels, each including a switching TFT 1510, a current controlling TFT 1511, and a first electrode 1512 electrically connected to a drain of the controlling TFT 1511. In addition, an insulator 1513 is
25 formed to cover an edge of the first electrode 1512. Here, a positive photosensitive acrylic resin film is used to form the insulator 1513.

[0376]

Besides, in order to obtain a favorable coverage, the insulator 1513 is formed to have a top portion or a bottom portion with a curved surface that has a curvature.
30 For example, in the case of using positive photosensitive acrylic as a material for the

insulator 1513, it is preferable that only a top portion of the insulator 1513 have a curved surface with a curvature radius (0.2 to 3 μm). In addition, any of a negative photosensitive material that becomes insoluble in an etchant by light and a positive photosensitive material that becomes soluble in an etchant by light can be used for the
5 insulator 1513. Further, it is possible to use not only organic substances but also inorganic substances as a material for the insulator 1513, for example, silicon oxide and silicon oxynitride can be used.

[0377]

On the first electrode 1512, a layer 1514 including a luminescent material and a
10 second electrode 1515 are formed. Here, as a material to be used for the first electrode 1512 that functions as an anode, it is preferable to use a material that has a large work function. For example, in addition to single layers such as a film including indium tin oxide, a film including indium tin oxide containing silicon oxide, a film including indium zinc oxide, a titanium nitride film, a chromium film, a tungsten film, a Zn film,
15 and a Pt film, laminated structures such as a laminate of a titanium nitride film and a film including aluminum as its main component and a three-layer structure of a titanium nitride film, a film including aluminum as its main component, and a titanium nitride film can be used. When a laminated structure is used, it is possible to have a lower resistance as a wiring, take favorable ohmic contact, and function as an anode.

20 [0378]

In addition, the layer 1514 including the luminescent material is formed by evaporation using an evaporation mask or by inkjet. The layer 1514 including the luminescent material includes an organometallic complex according to the present invention. As a material to be used in combination with the organometallic complex,
25 low molecular weight materials, middle molecular weight materials (including an oligomer and a dendrimer) or polymer materials may be used. In addition, as a material to be used for the layer including the luminescent material, it is often the case that an organic material is used for a single layer or a laminate. However, the present invention includes a structure in which an inorganic compound is used for a part of a
30 film including an organic compound.

[0379]

Further, as a material to be used for the second electrode (cathode) 1515 formed on the layer 1514 including the luminescent material, a material that has a small work function, for example, Al, Ag, Li, or Ca, an alloy thereof such as Mg:Ag, Mg:In, Al:Li, or a metal compound such as CaF_2 or CaN , may be used. In the case of transmitting light generated in the layer 1514 including the luminescent material through the second electrode 1515, it is preferable to use a laminate of a metal thin film that has a thinned film thickness and a transparent conductive film (for example, an alloy of indium oxide and tin oxide (ITO), an alloy of indium oxide and zinc oxide ($\text{In}_2\text{O}_3\text{-ZnO}$), or zinc oxide (ZnO)) as the second electrode (cathode) 1515.

[0380]

Further, the sealing substrate 1504 and the substrate 1509 are bonded with the sealing material 1505 to have a structure where a light-emitting element 1516 is provided in the space surrounded by the substrate 1509, the sealing substrate 1504, and the sealing material 1505. The space 1506 also includes a structure of filling with the sealing material 1505 in addition to a case of filling with an inert gas (for example, nitrogen or argon).

[0381]

It is to be noted that it is preferable to use an epoxy resin for the sealing material 1505. In addition, it is desirable to use a material that hardly allows permeation of moisture or oxygen. Further, as a material to be used for the sealing substrate 1504, a plastic substrate composed of FRP (Fiberglass-Reinforced Plastics), PVF (polyvinylfluoride), Mylar, polyester, acrylic, or the like can be used besides a glass substrate and a quartz substrate.

25 [0382]

As described above, a light-emitting device that has a light-emitting element according to the present invention can be obtained. In the above-described light-emitting device according to the present invention, the light-emitting element according to the present invention is excellent in luminous efficiency, and can be driven for a long time. Therefore, the light-emitting device has a long lifetime with low

30

power consumption.

[0383]

[Embodiment 10]

5 In the present example, various electric apparatuses completed by using a light-emitting device that has a light-emitting element according to the present invention will be described. Since a light-emitting device according to the present invention has a long lifetime with low power consumption, an electronic device using the light-emitting device can be also used for a long time by reducing, for example, power
10 for a display portion and a lighting portion.

[0384]

Electric devices manufactured by using a light-emitting device formed according to the present invention include a television, a video camera, a digital camera, a goggle-type display (head mount display), a navigation system, a sound reproduction
15 device (such as an in-car audio system or an audio set), a laptop personal computer, a game machine, a personal digital assistance (such as a mobile computer, a cellular phone, a portable game machine, or an electronic book), an image reproduction device equipped with a recording medium (specifically, a device equipped with a display device, which can reproduce a recording medium such as a digital versatile disc (DVD)
20 and display the image), and a lighting apparatus. Some specific examples of the electric devices will be described with reference to FIGS. 36A to 36E. The electronic devices using a light-emitting device according to the present invention are not limited to these exemplified specific examples.

[0385]

25 FIG. 36A is a display device, which includes a frame body 1600, a support 1601, a display portion 1602, a speaker portion 1603, and a video input terminal 1604. A light-emitting device formed according to the present invention is used for the display portion 1602 to manufacture the display device. The display device includes all devices for displaying information such as for a personal computer, for receiving TV
30 broad casting, and for displaying an advertisement.

[0386]

FIG. 36B is a laptop personal computer, which includes a main body 1700, a frame body 1701, a display portion 1702, a keyboard 1703, an external connection port 1704, and pointing mouse 1705. A light-emitting device that has a light-emitting element according to the present invention is used for the display portion 1702 to manufacture the laptop computer.

[0387]

FIG. 36C is a video camera, which includes a main body 1800, a display portion 1801, a frame body 1802, an external connection port 1803, a remote-control receiving portion 1804, an image receiving portion 1805, a battery 1806, a voice input portion 1807, operation keys 1808, and an eye piece 1809. A light-emitting device that has a light-emitting element according to the present invention is used for the display portion 1801 to manufacture the video camera.

[0388]

FIG. 36D is a desk lighting apparatus, which includes a lighting portion 1900, a shade 1901, a variable arm 1902, a support 1903, a pedestal 1904, and a power source 1905. A light-emitting device formed by using a light-emitting element according to the present invention is used for the lighting portion 1900 to manufacture the desk lighting apparatus. It is to be noted that the lighting apparatus includes a lighting apparatus to be fixed to the ceiling and a wall-hung lighting apparatus.

[0389]

FIG. 36E is a cellular phone, which includes a main body 2000, a frame body 2001, a display portion 2002, a voice input portion 2003, a voice output portion 2004, an operation key 2005, an external connection port 2006, and an antenna 2007. A light-emitting device that has a light-emitting element according to the present invention is used for the display portion 2002 to manufacture the cellular phone.

[0390]

As described above, an electric device that has a light-emitting device using a light-emitting element according to the present invention can be obtained. In addition, in each of the above-described electronic devices according to the present invention, the

light-emitting element according to the present invention is excellent in luminous efficiency, and can be driven for a long time. Therefore, the electronic devices can be driven for a long time with low power consumption, which is economical.

5 [0391]
[Embodiment 11]

In the present embodiment, a case of using a luminescent material according to the present invention and another luminescent material to form a white light-emitting element will be described.

10 [0392]

In order to form a white light-emitting element with the use of a luminescent material according to the present invention, it is necessary to provide a plurality of light-emitting regions between a first electrode and second electrode and control the luminescent color from each light-emitting region so as to obtain white light as a whole. However, when a light-emitting region including a luminescent material according to the present invention, that is, a red or reddish phosphorescent material, is formed so as to come in contact with another light-emitting region including another luminescent material, energy transfer occurs between the luminescent material, and there is a possibility that a phenomenon occurs, where the phenomenon is that light is emitted more strongly as for only the luminescent color of either one luminescent material while light is emitted more weakly as for the luminescent color of the other luminescent material. In order to improve this imbalance of the luminescent colors, a separation layer may be provided between the light-emitting regions. The separation layer is required to have a light-transmitting property, and may be formed by using an electron transporting material or a hole electron transporting material. Specifically, the electron transporting materials and hole transporting materials mentioned in the embodiment modes may be used.

[0393]

Next, FIG. 37 shows one example of the structure of a white light-emitting element in the case of providing two light-emitting regions. In FIG. 37, there are a first

30

light-emitting region 2102 and a second light-emitting region 2104 between a first electrode 2101 and a second electrode 2105, and there is a separation layer 2103 between the first light-emitting region 2102 and the second light-emitting region 2104. Reference numeral 2100 denotes a substrate. When a phosphorescent material according to the present invention is used for the first light-emitting region 2102, and a blue-green luminescent material is used for the second light-emitting region 2104, white light can be obtained as a whole.

[0394]

The blue-green luminescent material for forming the second light-emitting region 2104 includes fluorescent materials such as perylene, 2, 5, 8, 11 - tetra - tert - butylperylene (abbreviation: TBP), 4, 4' - bis (2 - diphenylvinyl) biphenyl (DPVBi), 4, 4' - bis [2 - (N - ethylcarbazole - 3 - yl) vinyl] biphenyl (abbreviation: BCzVBi), bis (2 - methyl - 8 - quinolinolato) - 4 - phenylphenolato - aluminum (abbreviation: BAlq), and bis (2 - methyl - 8 - quinolinolato) - chlorogallium (abbreviation: Gamq₂Cl), and phosphorescent materials such as bis [2 - (3, 5 - bis (trifluoromethyl) phenyl) pyridinato - N, C^{2'}] iridium (III) picolate (Ir(CF₃ppy)₂(pic)), bis [2 - (4', 6' - difluorophenyl) pyridinato - N, C^{2'}] iridium (III) acetylacetonate (FIr(acac)), and bis [2 - (4', 6' - difluorophenyl) pyridinato - N, C^{2'}] iridium (III) picolate (FIr(pic)).

[0395]

The structure shown in FIG. 37 will be described specifically. On the substrate 2100, ITO to serve as the first electrode 2101 is deposited so as to be 110 nm in film thickness.

[0396]

Next, the first light-emitting region 2102 is formed. Specifically, DNTPD that is a hole injecting material and α -NPD that is a hole transporting material are deposited to be 50 nm and 30 nm, respectively. After that, Ir(Fdpq)₂(acac) that is a red or reddish phosphorescent material according to the present invention and α -NPD are deposited by co-evaporation to be 30 nm in film thickness so that Ir(Fdpq)₂(acac) is included at 8 weight%.

[0397]

Next, CBP is deposited to be 5 nm in film thickness as the separation layer 2103. After that, the second light-emitting region 2104 is formed. Specifically, Ir(CF₃ppy)₂(pic) that is a blue-green phosphorescent material and CBP are deposited to be 25 nm in film thickness so that Ir(CF₃ppy)₂(pic) is included at 8 weight%. Then, BCP that is a hole blocking material (and an electron transporting material) is deposited to be 10 nm, and further, Alq₃ is deposited to be 20 nm as an electron transporting layer. After that, calcium fluoride (abbreviation: CaF₂) is deposited to be 1 nm in film thickness as an electron injecting layer.

[0398]

After that, Al is deposited so as to be 150 nm as the second electrode 2105.

[0399]

In accordance with this process, a white light-emitting element using a phosphorescent material according to the present invention and a blue-green phosphorescent material is obtained. In the structure of FIG. 37, a bipolar material is used for the separation layer 2103. However, a hole transporting material, an electron transporting material, a hole blocking material, and the like may be used without limitation to the bipolar material. In addition, although an example of providing two light-emitting elements is shown in the present embodiment, more light-emitting regions may be provided in order to obtain white light as a whole.

[0400]

Alternatively, in the case of using a blue-green fluorescent material to form a white light-emitting element, ITO is deposited to be 110 nm as the first electrode 2101, DNTPD that is a hole injecting material and α -NPD that is a hole transporting material are deposited respectively to be 50 nm and 30 nm, and for the first light-emitting region 2102, Ir(Fdpq)₂(acac) that is a red or reddish phosphorescent material according to the present invention and α -NPD are deposited by co-evaporation to be 30 nm in film thickness so that Ir(Fdpq)₂(acac) is included at 8 weight%. After that, CBP is deposited to be 5 nm as the separation layer 2103, and for the second light-emitting region 2104, perylene that is a blue-green fluorescent material and BAlq are deposited to be 25 nm in film thickness so that perylene is included at 1 weight%. Then, Alq₃ is

deposited to be 30 nm as an electron transporting layer. After that, CaF_2 is deposited to be 1 nm as an electron injecting layer, and finally, Al is deposited to be 150 nm as the second electrode 2105. In accordance with this process, a white light-emitting element using a red or reddish phosphorescent material and a blue-green fluorescent material
5 can be obtained.

[0401]

[Embodiment 12]

In the present embodiment, the structure of a white light-emitting element
10 using a phosphorescent material according to the present invention, which is different from the structure in Embodiment 11, will be described with reference to FIG. 38.

[0402]

In FIG. 38, there are a first light-emitting region 2202, a second light-emitting region 2204, and a third light-emitting region 2206 between a first electrode 2201 and a
15 second electrode 2207. Further, there is a carrier generation layer 2203 between the first light-emitting region 2202 and the second light-emitting region 2204, and there is a carrier generation layer 2205 between the second light-emitting region 2204 and the third light-emitting region 2206. When a phosphorescent material according to the present invention, a green or greenish luminescent material, and a blue or bluish
20 luminescent material are used respectively for the first light-emitting region 2202, the second light-emitting region 2204, and the third light-emitting region 2206.

[0403]

The blue or bluish luminescent material include fluorescent materials such as perylene, 2, 5, 8, 11 - tetra - tert - butylperylene (abbreviation: TBP), 1, 1, 4, 4 -
25 tetraphenyl - 1, 3 - butadiene (abbreviation: TPB), 9, 9' - bianthryl (abbreviation: BiAnt), 9, 10 - diphenylanthracene (abbreviation: DPA), 9, 10 - di (2 - naphthyl) anthracene (abbreviation: DNA), 9, 10 - di (2 - naphthyl) - 2 - tert - butylanthracene (abbreviation: t-BuDNA), and phosphorescent materials such as bis [2 - (4', 6' - difluorophenyl) pyridinato - N, $\text{C}^{2'}$] iridium (III) tetrakis (1 - pyrazolyl) borate (abbreviation: Flr₆).

30

[0404]

The green or greenish luminescent material include fluorescent materials such as coumarin 6, coumarin 545T, N, N' - dimethylquinacridone (abbreviation: DMQd), 5, 12 - diphenyltetracene (abbreviation: DPT), and tris (8 - quinolinolato) aluminum, and phosphorescent materials such as tris (2 - phenylpyridinato - N, C^{2'}) iridium (abbreviation: Ir(ppy)₃), bis (2 - phenylpyridinato - N, C^{2'}) iridium (III) acetylacetonate (abbreviation: Ir(ppy)₂(acac)), and bis [2 - (4 - methylphenyl) pyridinato - N, C^{2'}] iridium (III) acetylacetonate (abbreviation: Ir(tpy)₂(acac))

[0405]

In addition, a transparent conductive film can be used for the carrier generation layer. Specifically, an indium tin oxide (abbreviation: ITO), an indium tin oxide containing silicon, and an indium oxide including zinc oxide at 2 to 20 % can be given.

[0406]

The structure shown in FIG. 38 will be described specifically. On a substrate 2200, an ITO to serve as the first electrode 2201 is deposited to be 110 nm in film thickness. Specifically, as a hole injecting layer, molybdenum oxide and α -NPD are deposited by co-evaporation to be 50 nm in film thickness so that the mass ratio of molybdenum oxide to α -NPD is 1 : 0.25 (= α -NPD : molybdenum oxide), and α -NPD that is a hole transporting material is deposited to be 10 nm. Next, the first light-emitting region 2202 is formed. Specifically, Ir(Fdpq)₂(acac) that is a red or reddish phosphorescent material according to the present invention and Alq₃ are deposited by co-evaporation to be 37.5 nm in film thickness so that Ir(Fdpq)₂(acac) is included at 8 weight%. Alq₃ is deposited to be 27.5 nm as an electron transporting layer, and as an electron injecting layer, BCP and Li are deposited by co-evaporation to be 10 nm in film thickness so that the mass ratio of Li to BCP is 1 : 0.005 (= BCP: Li). Then, ITO is deposited to be 20 nm in film thickness as the carrier generation layer (a transparent conductive film) 2203.

[0407]

On the transparent conductive film 2203, the second light-emitting region 2204 is formed. Specifically, as a hole injecting layer, α -NPD and molybdenum oxide are deposited by co-evaporation to be 50 nm in film thickness so that the mass ratio of

molybdenum oxide to α -NPD is 1 : 0.25 (= α -NPD : molybdenum oxide), and α -NPD is deposited to be 10 nm as a hole transporting material. Then, as a green or greenish luminescent material for the second light-emitting region 2204, coumarin 6 and Alq₃ are deposited by co-evaporation to be 37.5 nm in film thickness. Then, Alq₃ is deposited
5 to be 27.5 nm as an electron transporting layer, and as an electron injecting layer, and BCP and Li are deposited by co-evaporation to be 10 nm in film thickness so that the mass ratio of Li to BCP is 1 : 0.005 (= BCP: Li). Then, ITO is deposited to be 20 nm in film thickness as the carrier generation layer (a transparent conductive film) 2205.

[0408]

10 On the transparent conductive film 2205, the third light-emitting region 2206 is formed in a similar way. Specifically, as a hole injecting layer, α -NPD and molybdenum oxide are deposited by co-evaporation to be 50 nm in film thickness so that the mass ratio of molybdenum oxide to α -NPD is 1 : 0.25 (= α -NPD : molybdenum oxide), and α -NPD that is a hole transporting material is deposited to be 10 nm. Then,
15 as a blue or bluish luminescent material for the third light-emitting region 2206, t-BuDNA is deposited to be 37.5 nm in film thickness. Then, Alq₃ is deposited to be 27.5 nm as an electron transporting layer, and as an electron injecting layer, BCP and Li are deposited by co-evaporation to be 10 nm in film thickness so that the mass ratio of Li to BCP is 1 : 0.005 (= BCP: Li). Then, as the second electrode 2207, aluminum is
20 deposited to be 200 nm in film thickness. In this way, a white light-emitting element into which the red or reddish phosphorescent material according to the present invention is introduced can be obtained.

[0409]

Although an example of providing three light-emitting regions is shown in the
25 present embodiment, two light-emitting regions, or four or more light-emitting region may be provided in order to obtain white light as a whole.

[0410]

[Embodiment 13]

30 In the present embodiment, the structure of a light-emitting element using an

organometallic complex according to the present invention as a luminescent material and a manufacturing method thereof will be described with reference to FIG. 39.

[0411]

On a substrate 2300, indium tin oxide was deposited by sputtering to form a
5 first electrode 2301. The film thickness was made to be 110 nm.

[0412]

Next, the substrate 2300 on which the first electrode 2301 was formed was fixed in a substrate holder provided in a vacuum deposition system so that the surface at which the first electrode 2301 was formed was made down.

10 [0413]

Next, on the first electrode 2301, copper phthalocyanine was deposited by evaporation using resistance heating so as to be 20 nm in film thickness to form a hole injecting layer 2302.

[0414]

15 Next, on the hole injecting layer 2302, α -NPD was deposited by evaporation using resistance heating so as to be 40 nm in film thickness to form a hole transporting layer 2303.

[0415]

Next, on the hole transporting layer 2303, $\text{Ir}(\text{Fdpq})_2(\text{acac})$ and TPAQn were
20 deposited by co-evaporation so as to be 30 nm in film thickness to form a light-emitting layer 2304. Here, $\text{Ir}(\text{Fdpq})_2(\text{acac})$ and TPAQn were deposited so that $\text{Ir}(\text{Fdpq})_2(\text{acac})$ was included at a rate of 8 weight% in a layer composed of TPAQn. This rate makes $\text{Ir}(\text{Fdpq})_2(\text{acac})$ dispersed in the layer composed of TPAQn. It is to be noted that co-evaporation is an evaporation method in which evaporation is performed
25 simultaneously from a plurality of evaporation sources.

[0416]

Next, on the light-emitting layer 2304, Alq_3 was deposited by evaporation using resistance heating so as to be 30 nm in film thickness to form an electron transporting layer 2305.

30 [0417]

Next, on the electron transporting layer 2305, calcium fluoride was deposited by evaporation using resistance heating so as to be 2 nm in film thickness to form an electron injecting layer 2306.

[0418]

5 Next, on the electron injecting layer 2306, aluminum was deposited by evaporation using resistance heating so as to be 150 nm in film thickness to form a second electrode 2307.

[0419]

10 A voltage was applied to the thus manufactured light-emitting element so that the potential of the first electrode 2301 was higher than the potential of the second electrode 2307. Then, light was emitted with a luminance of 466 cd/m^2 when a voltage of 7.6 V was applied. The current efficiency in this case was 1.56 cd/A. Further, the emission spectrum has a peak at 652 nm. FIG. 40 shows the emission spectrum. In addition, the element exhibits CIE chromaticity coordinates of $(x, y) =$
15 $(0.65, 0.33)$.

[0420]

As described above, a light-emitting element that is capable of providing favorable red or reddish luminescence with favorable chromaticity can be obtained by using an organometallic complex according to the present invention. In addition, when
20 a light-emitting layer is formed by combining an organometallic complex according to the present invention with a quinoxaline derivative as the light-emitting element in the present embodiment, the organometallic complex can be made to produce luminescence more efficiently.

[0421]

25 It is to be noted that materials to be used for manufacturing a light-emitting element according to the present invention with the use of an organometallic complex according to the present invention are not to be considered limited to the materials mentioned above, and the materials mentioned in Embodiment mode and another known materials may be used in addition to the materials mentioned in the present
30 embodiment. In addition, the layered structure of the light-emitting element is not

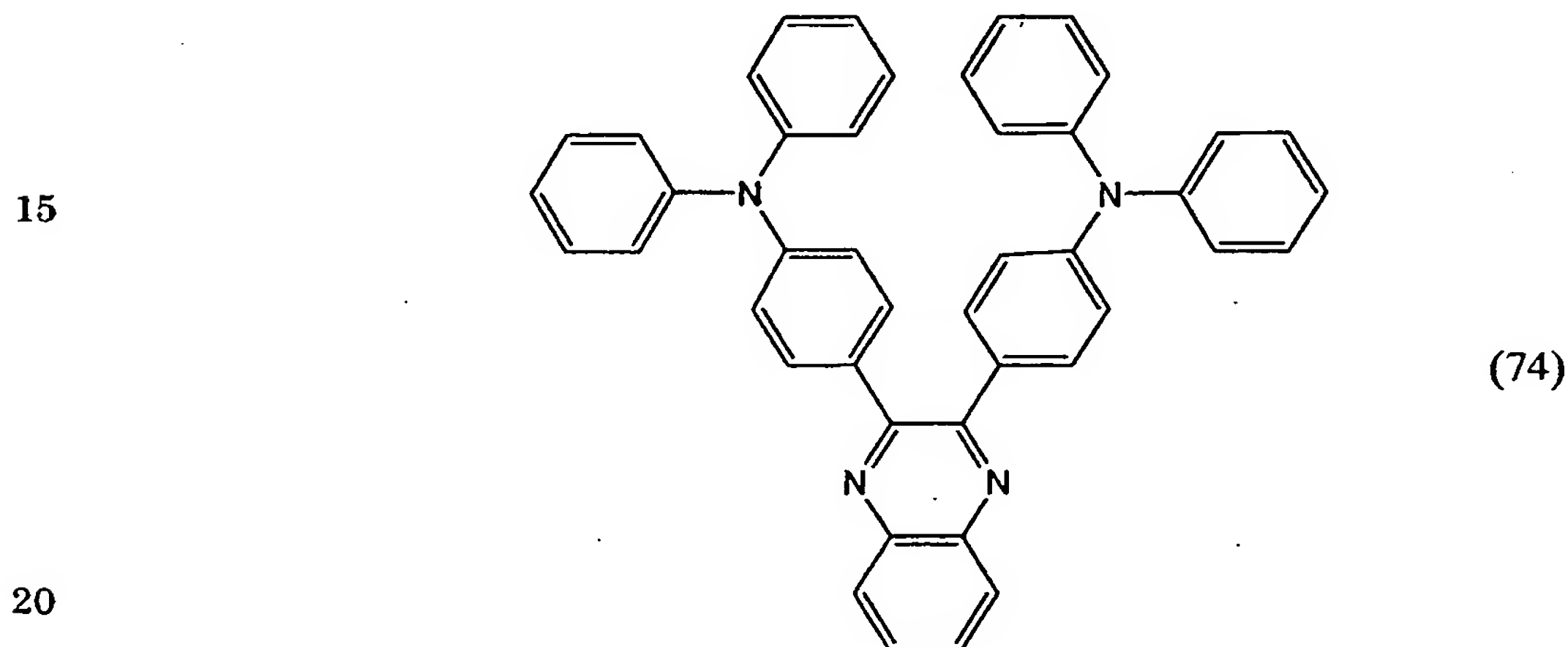
limited to the structure described in the present embodiment, either, and may be changed appropriately. Further, a method for manufacturing the light-emitting element is not particularly limited, either. An electrode to serve as an anode may be manufactured first as in the present embodiment, or an electrode to serve as a cathode
5 may be manufactured first.

[0422]

<Synthesis Example of TPAQn>

TPAQn used in Embodiment 13 is a novel material represented by the
10 following structure formula (74). A synthesis method of a quinoxaline derivative represented by the following formula (74) will be described here.

[0423]



[0424]

<Synthesis of 2, 3 - bis (4 - bromophenyl) quinoxaline>

First, 10 g (27.4 mmol) of 4 - bromobenzil and 3.5 g (33.5 mmol) o -
25 phenylenediamine were put in a 500 mL recovery flask, and held at reflux for 8 hours in chloroform. Then, after cooling to room temperature, remaining o - phenylenediamine was removed by column chromatography to obtain 2, 3 - bis (4 - bromophenyl) quinoxaline.

[0425]

30 <Synthesis of TPAQn>

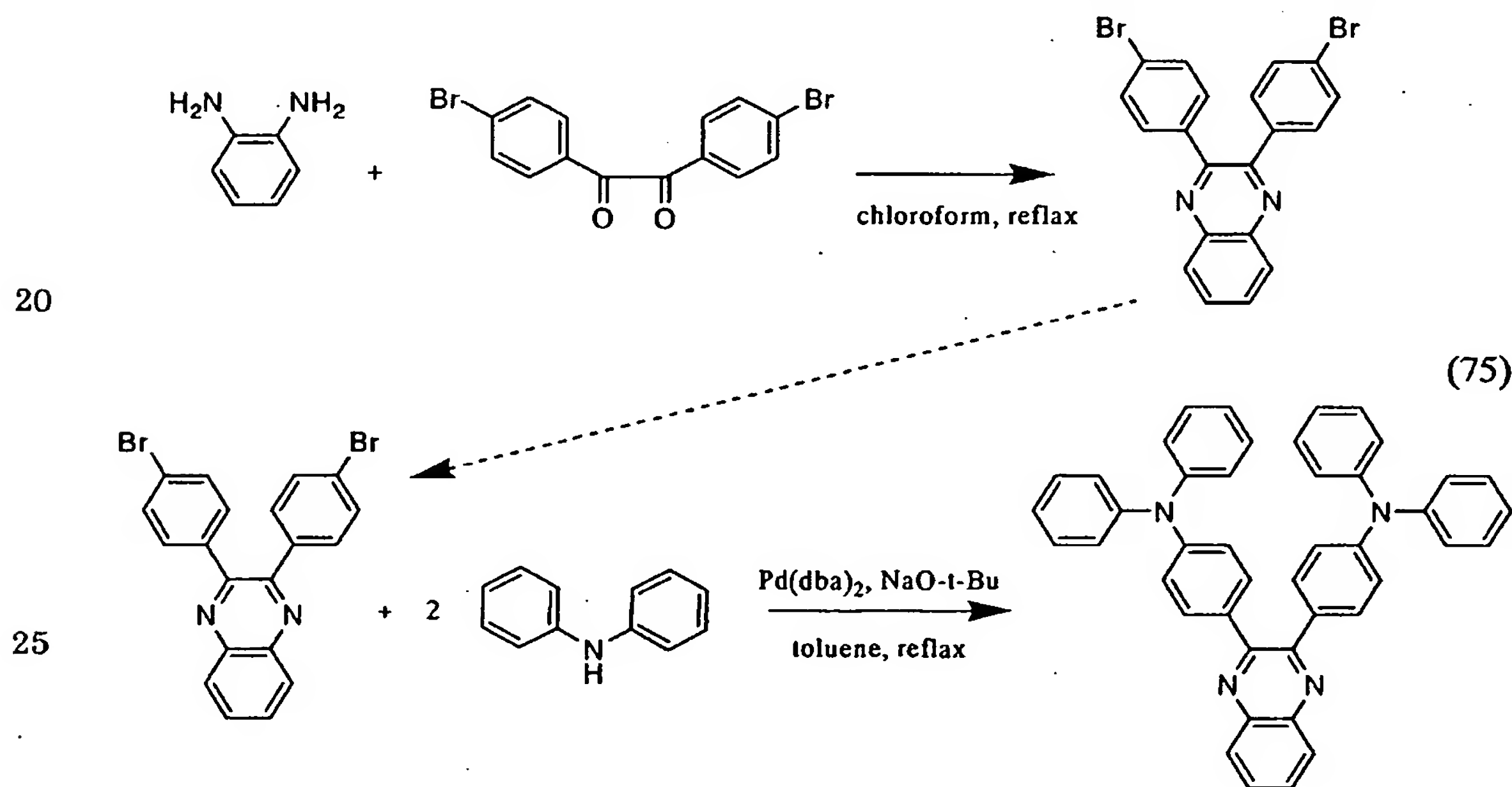
Further, 4.40 g (10.0 mmol) of the obtained 2, 3 - bis (4 - bromophenyl) quinoxaline was put in a three neck flask, and dissolved in 75 mL of toluene in a nitrogen gas stream. Then, 0.22 g (0.2 mmol) of $\text{Pd}(\text{dba})_2$, 2.88 g (30 mmol) of NaO-t-Bu , and 3.46 g (20.4 mmol) of diphenylamine were added, 1.8 mL of a 10 wt% hexane solution of tri (t - butylphosphine) was further added, and stirring on heating was performed at 80°C for 8 hours.

[0426]

Then, after cooling to room temperature, water was added to complete the reaction, and extraction with chloroform was performed. Further, after washing with a saturated aqueous solution of sodium chloride, drying with MgSO_4 was performed. After that, recrystallization from the chloroform was performed to obtain 2, 3 - bis (4 - diphenylaminophenyl) quinoxaline (abbreviation: TPAQn) (yellow-green crystal, yield: 2.7 g (44 %)).

[0427]

The synthesis scheme (75) of the synthesis described above is as follows.



[0428]

FIG. 41 shows a ^1H -NMR chart of TPAQn obtained by the synthesis described

above.

[0429]

Further, the thermal decomposition temperature of the obtained TPAQn was 411°C. The measurement was performed by Thermogravimetry/Differential Thermal
5 Analysis simultaneous measurement system (from Seiko Instruments Inc., TG/DTA-320).

[0430]

[Embodiment 14]

10 In the present embodiment, the structure of a light-emitting element using the organometallic complex synthesized in Synthesis Embodiment 3 as a luminescent material and a manufacturing method thereof will be described with reference to FIG. 42.

[0431]

15 First, on a substrate 2400, indium tin oxide including silicon oxide was deposited by sputtering to form a first electrode 2401. The film thickness was made to be 110 nm.

[0432]

20 Next, the substrate 2400 on which the first electrode 2401 was formed was fixed in a substrate holder provided in a vacuum deposition system so that the surface at which the first electrode 2401 was formed was made down.

[0433]

25 Then, on the first electrode 2401, 4, 4' - bis [N - {4 - (N, N - di - m - tolylamino) phenyl} - N - phenylamino] biphenyl (abbreviation: DNTPD) was deposited by evaporation using resistance heating so as to be 50 nm in film thickness to form a hole injecting layer 2402.

[0434]

30 Next, on the hole injecting layer 2402, α -NPD was deposited by evaporation using resistance heating so as to be 10 nm in film thickness to form a hole transporting layer 2403.

[0435]

Further, on the hole transporting layer 2403, $\text{Ir}(\text{Fdpq})_2(\text{pic})$ and TPAQn were deposited by co-evaporation so as to be 30 nm in film thickness to form a light-emitting layer 2404. Here, the mass ratio of $\text{Ir}(\text{Fdpq})_2(\text{pic})$ to TPAQn was made to be 1 : 0.05
5 (= TPAQn : $\text{Ir}(\text{Fdpq})_2(\text{pic})$). This ratio makes $\text{Ir}(\text{Fdpq})_2(\text{pic})$ dispersed in a layer composed of TPAQn. It is to be noted that co-evaporation is an evaporation method in which evaporation is performed simultaneously from a plurality of evaporation sources in one processing room.

[0436]

10 Next, on the light-emitting layer 2404, BAq was deposited by evaporation using resistance heating so as to be 10 nm in film thickness to form a hole blocking layer 2405.

[0437]

Next, on the hole blocking layer 2405, Alq_3 was deposited by evaporation
15 using resistance heating so as to be 50 nm in film thickness to form an electron transporting layer 2406.

[0438]

Next, on the electron transporting layer 2406, calcium fluoride was deposited by evaporation using resistance heating so as to be 1 nm in film thickness to form an
20 electron injecting layer 2407.

[0439]

Next, on the electron injecting layer 2407, aluminum was deposited by evaporation using resistance heating so as to be 200 nm in film thickness to form a second electrode 2408.

25 [0440]

When a voltage was applied to the thus manufactured light-emitting element so that the potential of the first electrode 2401 was higher than the potential of the second electrode 2408, it was determined that light was emitted with a luminance of 460 cd/m^2 when a voltage of 11.0 V was applied. The current efficiency in this case was 3.2 cd/A.
30 Further, the emission spectrum has a peak at 622 nm. FIG. 43 shows the emission

spectrum. In addition, the element exhibits CIE chromaticity coordinates of $(x, y) = (0.68, 0.32)$.

[0441]

As described above, a light-emitting element that is capable of providing
5 favorable red or reddish luminescence with favorable chromaticity can be obtained by using an organometallic complex according to the present invention.

[0442]

It is to be noted that the light-emitting element in the present embodiment has the hole blocking layer 2405 provided between the light-emitting layer 2404 and the
10 electron transporting layer 2406. The hole blocking layer 2405 has a favorable electron transporting property, can prevent the excitation energy of $\text{Ir}(\text{Fdpq})_2(\text{pic})$ excited in the light-emitting layer 2404 from transferring into the electron transporting layer 2406, and has a function of blocking transfer of holes from the light-emitting layer 2404 to the electron transporting layer 2406. Therefore, the luminous efficiency is
15 improved by providing the hole blocking layer. The hole blocking layer can be formed by using a material that has a larger energy gap and a larger ionization potential among materials that can be used for forming an electron transporting layer, such as BALq . As described above, in addition to an electron transporting layer or a hole transporting layer, various functional layers may be provided between a light-emitting layer and an
20 electrode.

[0443]

[Embodiment 15]

The present embodiment is an example of manufacturing a light-emitting
25 element in the same way as in Embodiment 14 except changing TPAQn in the light-emitting layer 2404 in Embodiment 14 to CBP .

[0444]

When a voltage was applied to this light-emitting element so that the potential of the first electrode 2401 was higher than the potential of the second electrode 2408, it
30 was determined that light was emitted with a luminance of 480 cd/m^2 when a voltage of

12.4 V was applied. The current efficiency in this case was 3.0 cd/A. Further, the emission spectrum has a peak at 622 nm. FIG. 44 shows the emission spectrum. It is to be noted that the horizontal axis and the vertical axis respectively show a wavelength (nm) and emission intensity (a. u.) in FIG. 44. In addition, the elements exhibits CIE chromaticity coordinates of $(x, y) = (0.66, 0.33)$.

[0445]

As described above, a light-emitting element that is capable of providing favorable red or reddish luminescence with favorable chromaticity can be obtained by using an organometallic complex according to the present invention.

10

[0446]

[Embodiment 16]

In the present embodiment, the structure of a light-emitting element using the organometallic complex synthesized in Synthesis Embodiment 4 as a luminescent material and a manufacturing method thereof will be described with reference to FIG. 42.

15

[0447]

First, on a substrate 2400, indium tin oxide including silicon oxide was deposited by sputtering to form a first electrode 2401. The film thickness was made to be 110 nm.

20

[0448]

Next, the substrate 2400 on which the first electrode 2401 was formed was fixed in a substrate holder provided in a vacuum deposition system so that the surface at which the first electrode 2401 was formed was made down.

25

[0449]

Then, on the first electrode 2401, 4, 4' - bis [N - {4 - (N, N - di - m - tolylamino) phenyl} - N - phenylamino] biphenyl (abbreviation: DNTPD) was deposited by evaporation using resistance heating so as to be 50 nm in film thickness to form a hole injecting layer 2402.

30

[0450]

Next, on the hole injecting layer 2402, α -NPD was deposited by evaporation using resistance heating so as to be 10 nm in film thickness to form a hole transporting layer 2403.

[0451]

5 Further, on the hole transporting layer 2403, $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ and CBP were deposited by co-evaporation so as to be 30 nm in film thickness to form a light-emitting layer 2404. Here, the mass ratio of $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ to CBP was made to be 1 : 0.025 (=CBP : $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$). This ratio makes $\text{Ir}(3, 5 - \text{Fdpq})_2(\text{acac})$ dispersed in a layer composed of CBP. It is to be noted that
10 co-evaporation is an evaporation method in which evaporation is performed simultaneously from a plurality of evaporation sources in one processing room.

[0452]

Next, on the light-emitting layer 2404, BCP was deposited by evaporation using resistance heating so as to be 10 nm in film thickness to form a hole blocking
15 layer 2405.

[0453]

Next, on the hole blocking layer 2405, Alq_3 was deposited by evaporation using resistance heating so as to be 20 nm in film thickness to form an electron transporting layer 2406.

20 [0454]

Next, on the electron transporting layer 2406, calcium fluoride was deposited by evaporation using resistance heating so as to be 1 nm in film thickness to form an electron injecting layer 2407.

[0455]

25 Next, on the electron injecting layer 2407, aluminum was deposited by evaporation using resistance heating so as to be 200 nm in film thickness to form a second electrode 2408.

[0456]

When a voltage was applied to the thus manufactured light-emitting element so
30 that the potential of the first electrode 2401 was higher than the potential of the second

electrode 2408, it was determined that light was emitted with a luminance of 520 cd/m² when a voltage of 10.2 V was applied. The current efficiency in this case was 0.98 cd/A. Further, the emission spectrum has a peak at 664 nm. FIG. 45 shows the emission spectrum. In addition, the element exhibits CIE chromaticity coordinates of
5 (x, y) = (0.71, 0.28).

[0457]

As described above, a light-emitting element that is capable of providing favorable red or reddish luminescence with favorable chromaticity can be obtained by using an organometallic complex according to the present invention.

10

[0458]

[Embodiment 17]

In the present embodiment, a light-emitting element was manufactured in the same way as in Embodiment 16 except changing CBP in the light-emitting layer 2404
15 and BCP in the hole blocking layer 2405 in Embodiment 16 respectively to Alq₃ and BAlq.

[0459]

When a voltage was applied to this light-emitting element so that the potential of the first electrode 2401 was higher than the potential of the second electrode 2408, it
20 was determined that light was emitted with a luminance of 460 cd/m² when a voltage of 10.0 V was applied. The current efficiency in this case was 1.2 cd/A. Further, the emission spectrum has a peak at 665 nm. FIG. 46 shows the emission spectrum. It is to be noted that the horizontal axis and the vertical axis respectively show a wavelength (nm) and emission intensity (a. u.) in FIG. 46. In addition, the element exhibits CIE
25 chromaticity coordinates of (x, y) = (0.69, 0.30).

[0460]

As described above, a light-emitting element that is capable of providing favorable red or reddish luminescence with favorable chromaticity can be obtained by using an organometallic complex according to the present invention.

30

[0461]

Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be understood that various changes and modifications will be apparent to those skilled in the art. Therefore, 5 unless such changes and modifications depart from the scope of the present invention hereinafter defined, they should be construed as being included therein.

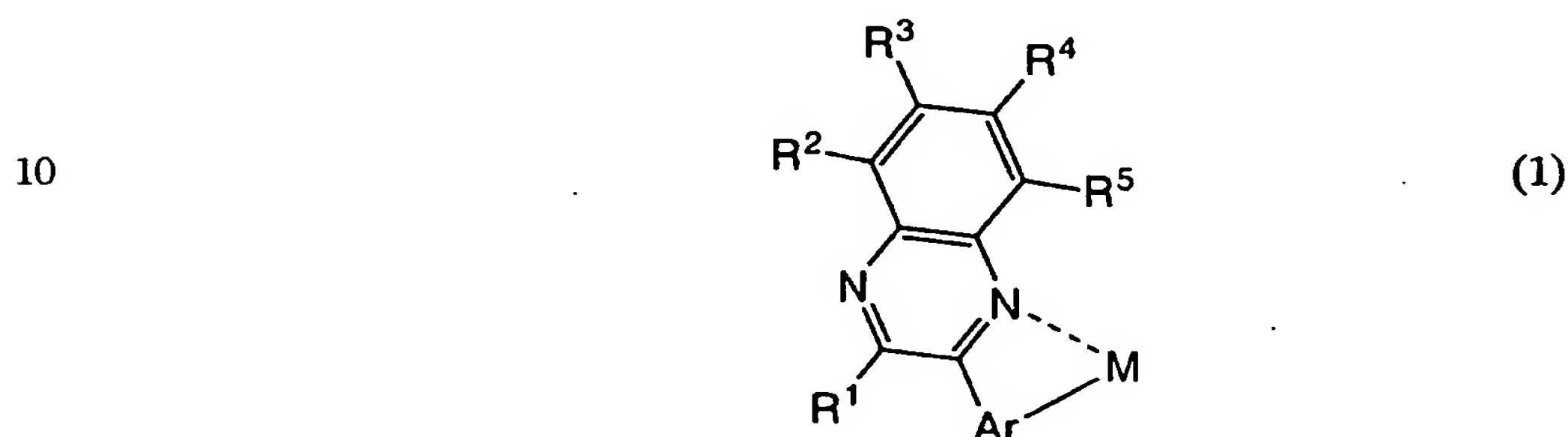
[0462]

This application is based on Japanese Patent Application serial no. 10 2004-151035 filed in Japan Patent Office on May 20, 2004, Japanese Patent Application serial no. 2004-226382 filed in Japan Patent Office on August 3, 2004 and Japanese Patent Application serial no. 2004-231742 filed in Japan Patent Office on August 6, 2004, the entire contents of which are hereby incorporated by reference.

CLAIMS

1. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

5 wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (1) and a compound that has a larger energy gap than the organometallic complex, and



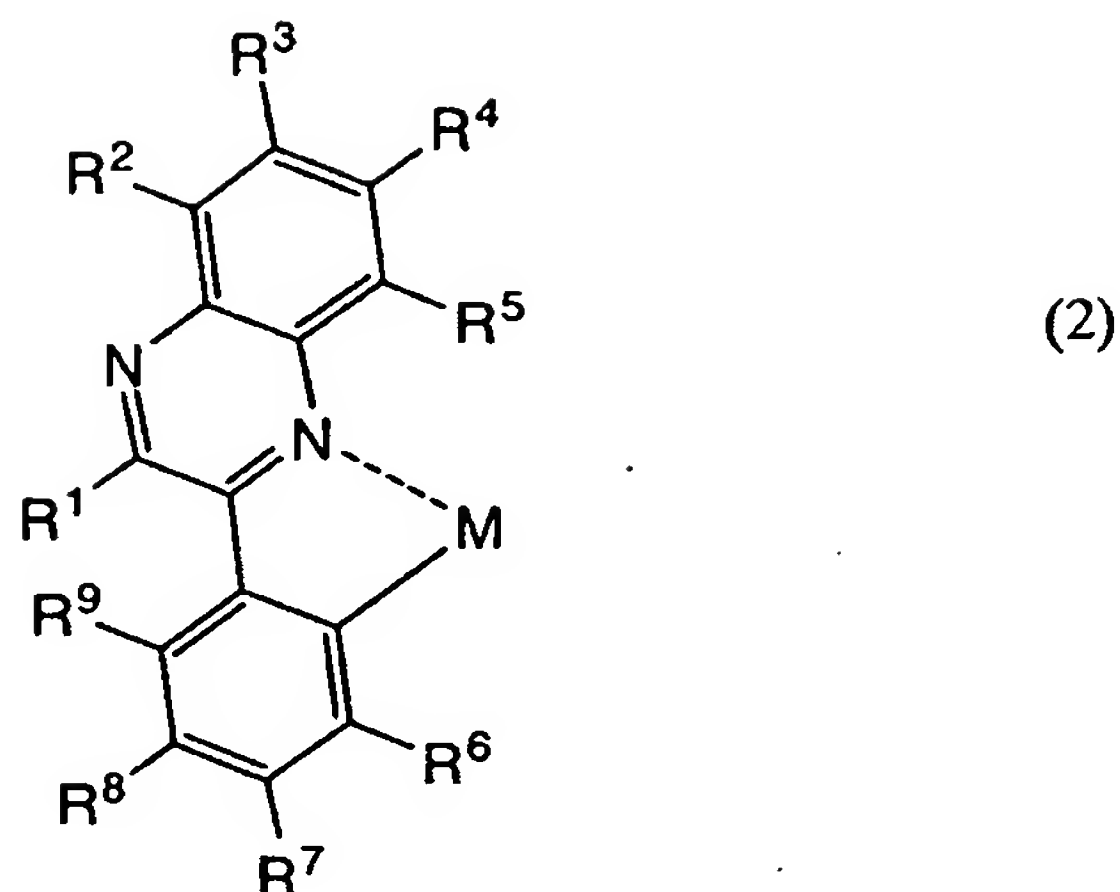
15 wherein each of R^1 to R^5 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10.

20 2. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (2) and a compound that has a larger energy gap than the organometallic complex, and

25

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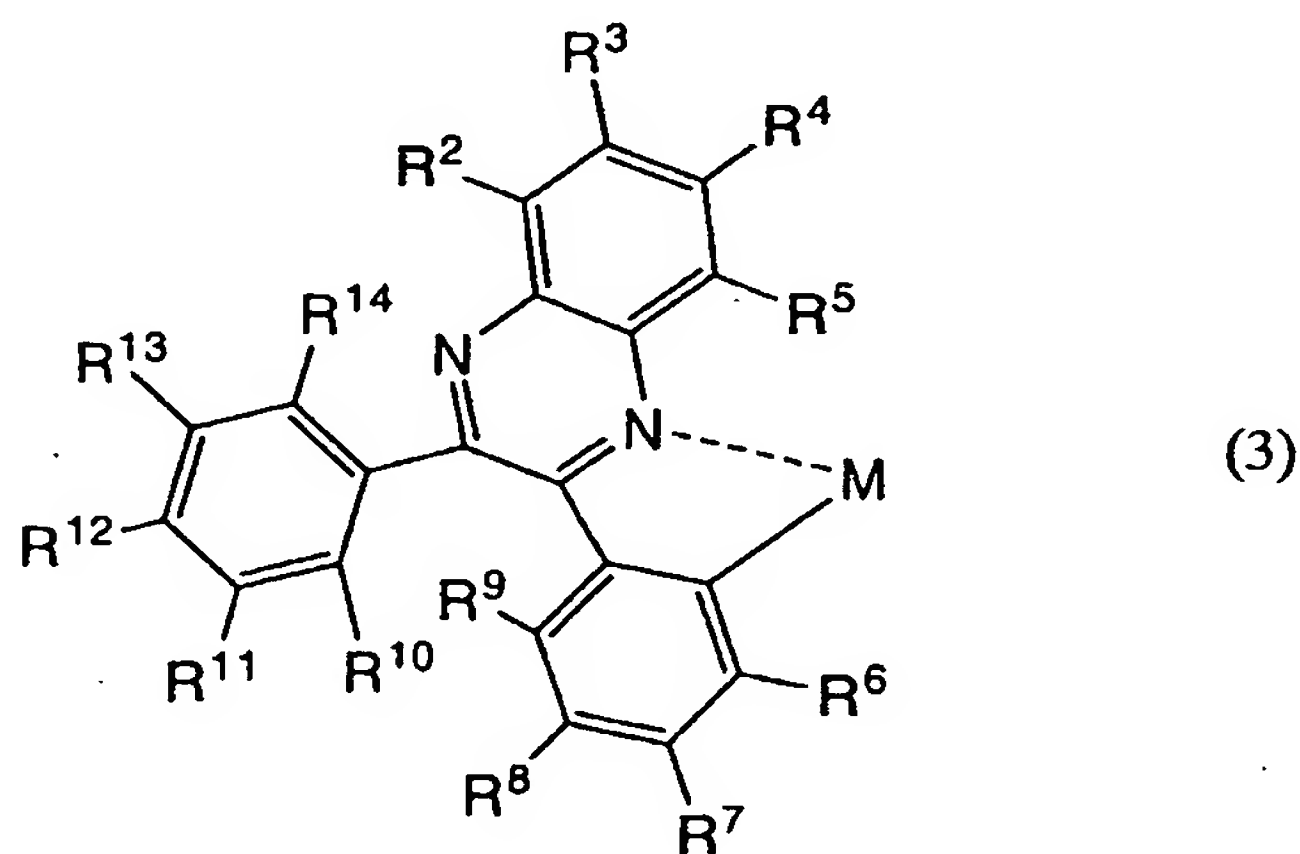
10 wherein each of R^1 to R^9 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, at least one of R^6 to R^9 is an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10.

15

3. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (3) and a compound that has a larger energy gap than the organometallic complex, and

20



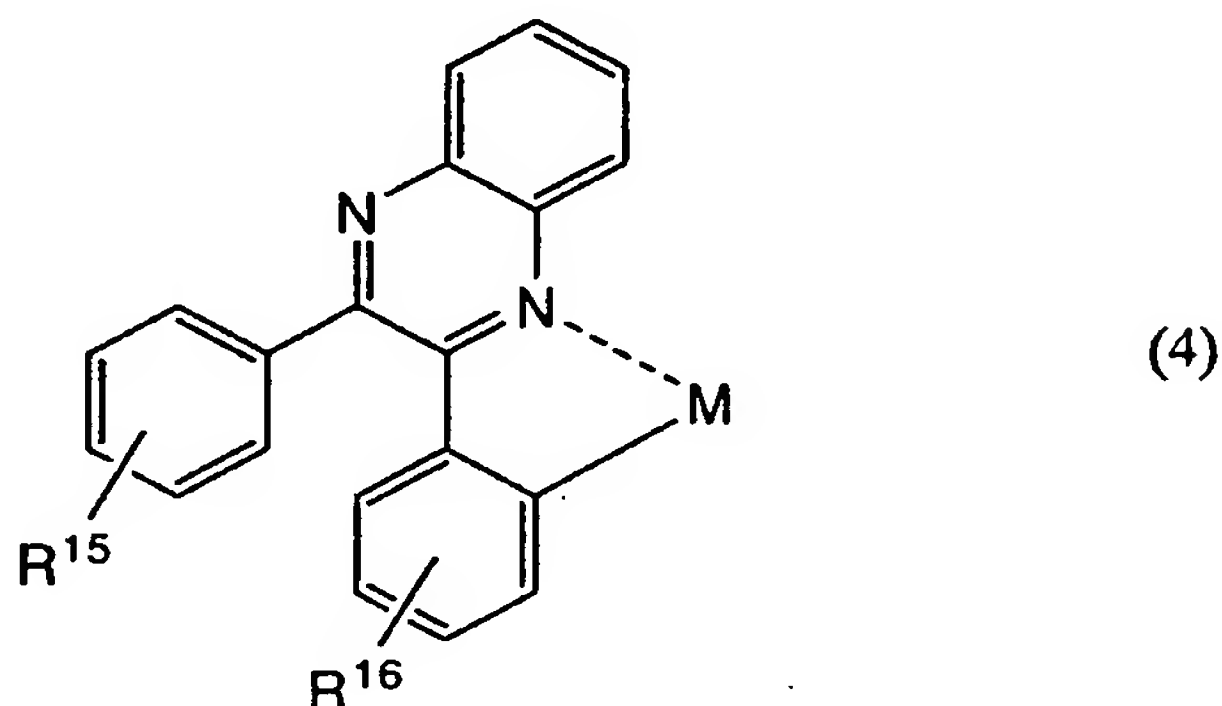
30 wherein each of R^2 to R^{14} is selected from the group consisting of hydrogen, a

halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10.

5 4. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (4) and a compound that has a larger energy gap than the organometallic complex, and

10



wherein each of R^{15} and R^{16} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10.

20

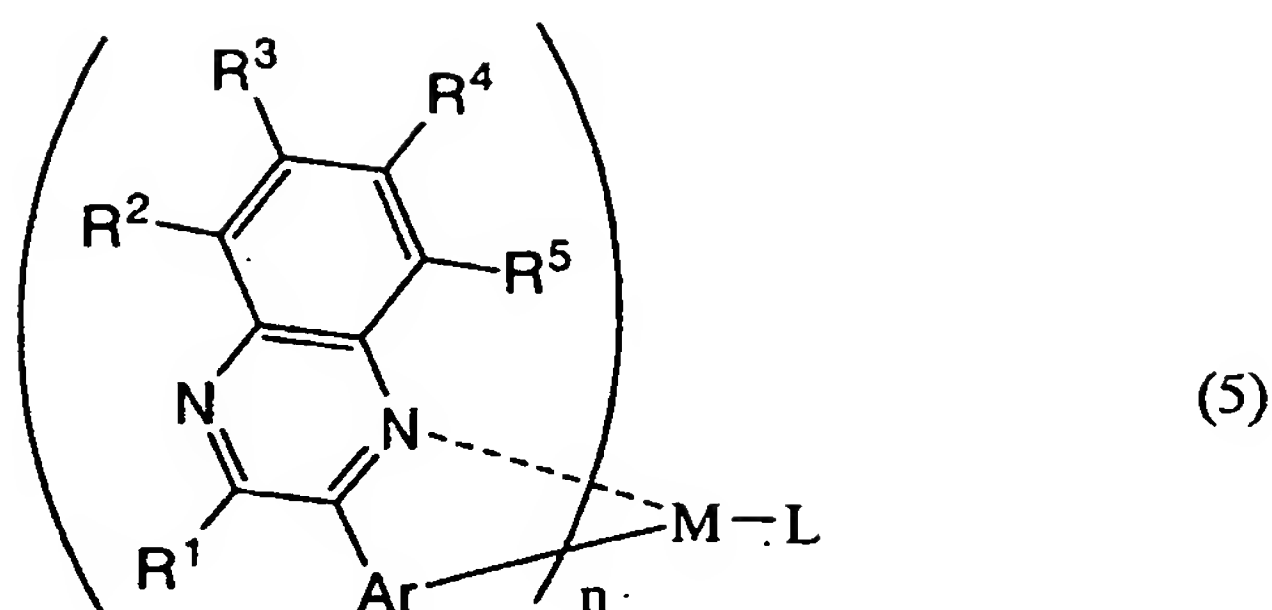
5. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (5) and a compound that has a larger energy gap than the organometallic complex, and

25

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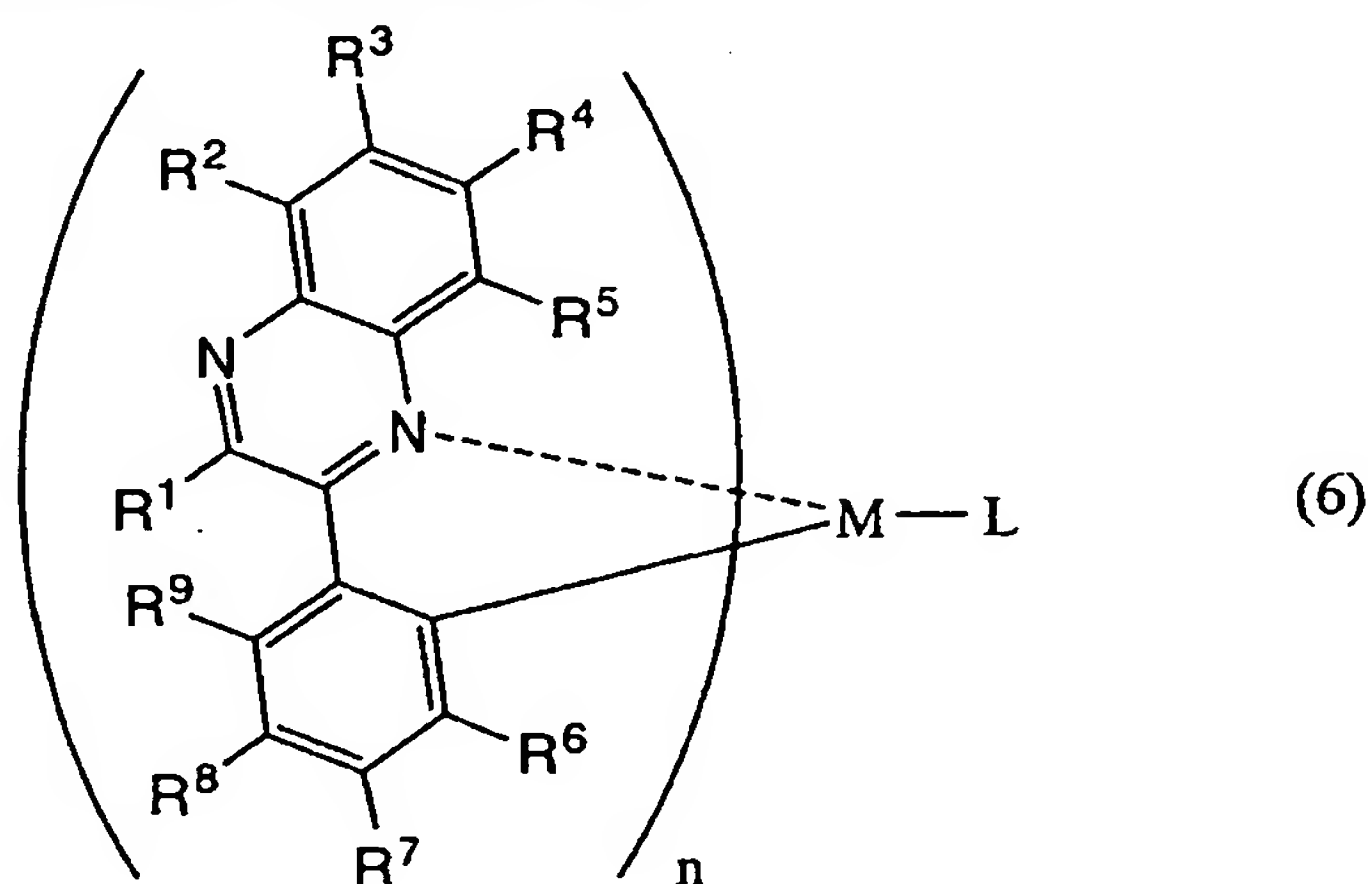


wherein each of R^1 to R^5 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

6. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (6) and a compound that has a larger energy gap than the organometallic complex, and

20



25

wherein each of R^1 to R^9 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a

30

cyano group, and a heterocyclic group, at least one of R^6 to R^9 is an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

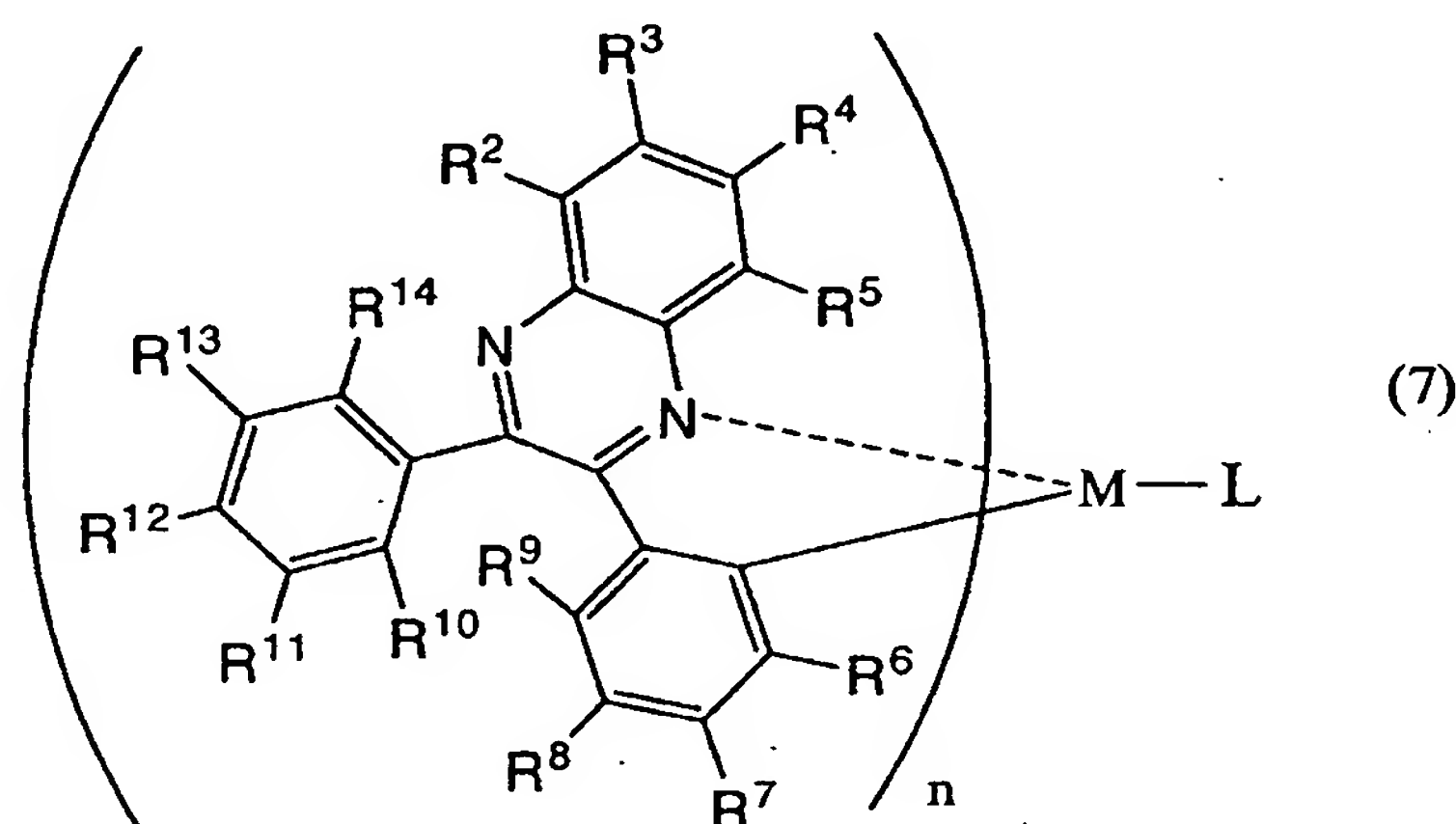
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7. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (7) and a compound that has a larger energy gap than the organometallic complex, and

10

15



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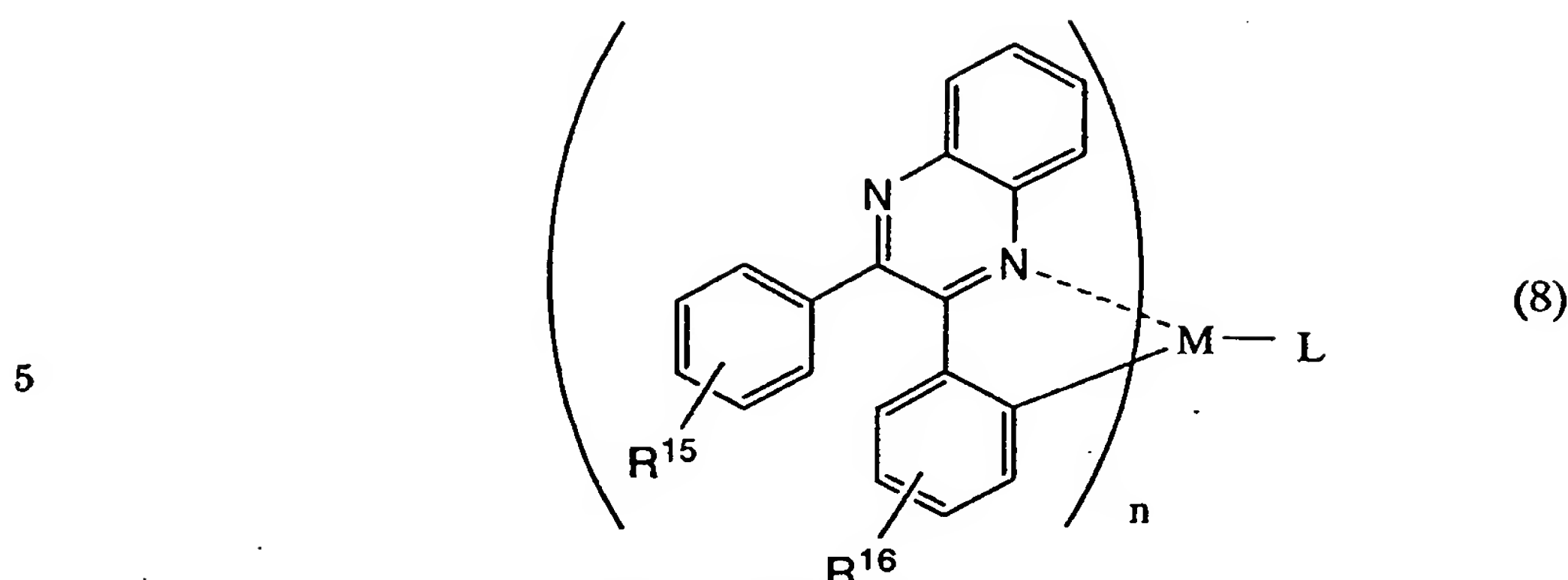
wherein each of R^2 to R^{14} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, and a heterocyclic group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

25

8. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (8) and a compound that has a larger energy gap than the organometallic complex, and

30

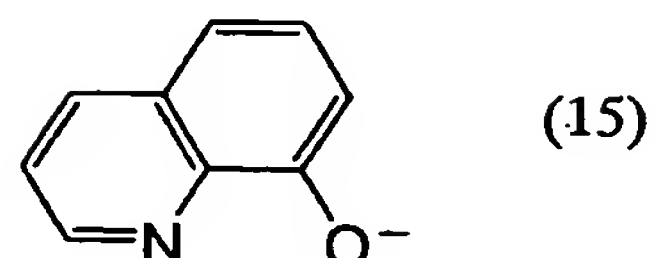
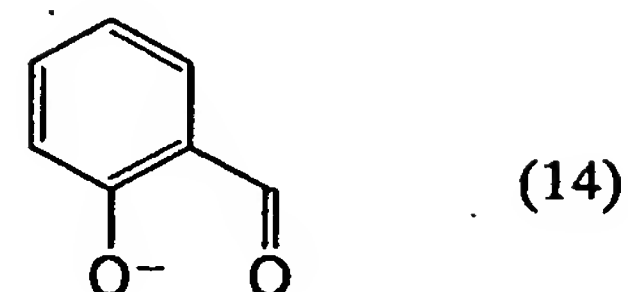
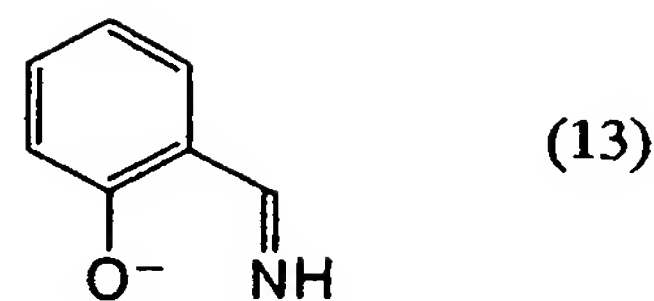
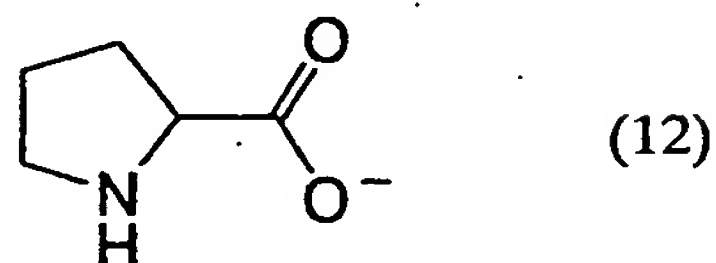
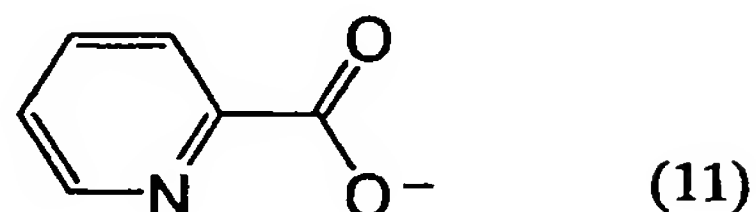
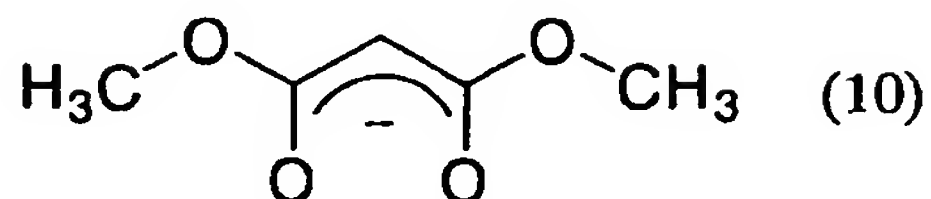
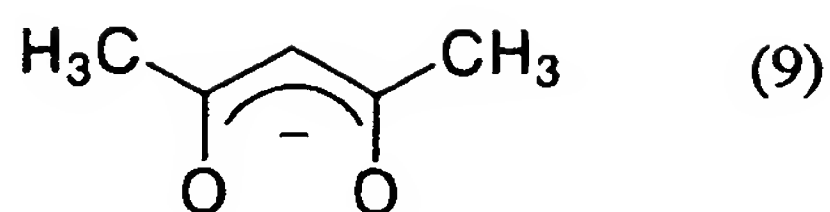


wherein each of R^{15} and R^{16} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

9. The light-emitting element according to any one of claims 1 to 8, wherein the compound that has the larger energy gap than the organometallic complex is one of 4, 4' - bis [N - (1 - naphthyl) - N - phenylamino] - biphenyl and tris (8 - quinolinolato) aluminum.

10. The light-emitting element according to any one of claims 5 to 8, wherein the anionic ligand L is one of an anionic ligand having a β -diketone structure, an anionic bidentate ligand having a carboxyl group, and an anionic bidentate ligand having a phenolic hydroxyl group.

11. The light-emitting element according to any one of claims 5 to 8, wherein the anionic ligand L is a ligand represented by any one of the following formulas (9) to (15).



15 12. The light-emitting element according to any one of claims 1 to 8, wherein
 the light-emitting layer includes the organometallic complex and one of a first
 compound that has a larger energy gap than the organometallic complex and has an
 electron mobility of 10^{-6} cm²/Vs or more and a second compound that has a larger
 energy gap than the organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or
 20 more.

25 13. The light-emitting element according to any one of claims 1 to 8, wherein
 the light-emitting layer includes the organometallic complex, a first compound that has
 a larger energy gap than the organometallic complex and has an electron mobility of
 10^{-6} cm²/Vs or more, and a second compound that has a larger energy gap than the
 organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or more.

30 14. The light-emitting element according to claim 12, wherein the first
 compound is a metal complex, and the second compound is an aromatic amine
 compound.

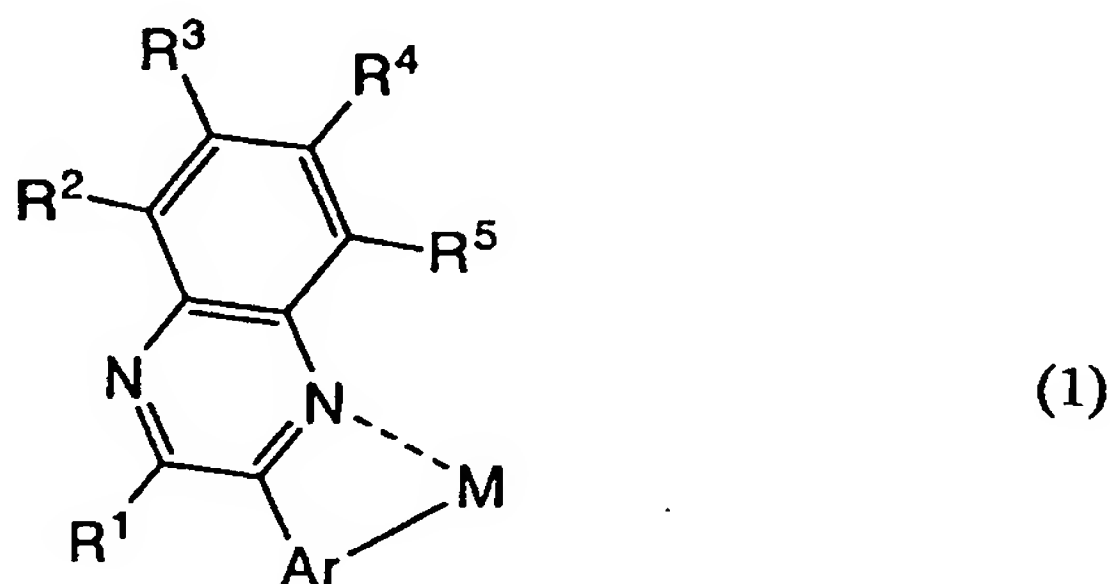
15. The light-emitting element according to claim 13, wherein the first compound is a metal complex, and the second compound is an aromatic amine compound.

5

16. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (1) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

15



wherein each of R¹ to R⁵ is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having an electron-withdrawing group, and M is one of an element of Group 9 and an element of Group 10.

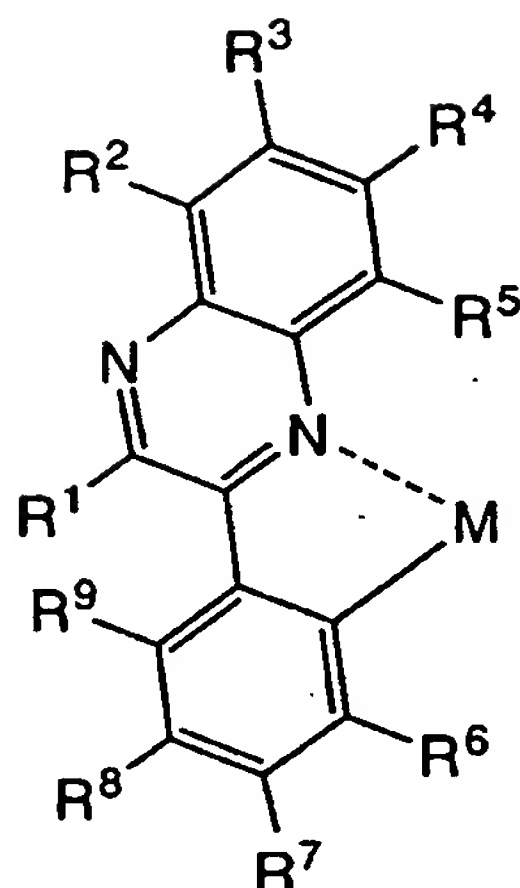
17. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (2) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

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(2)

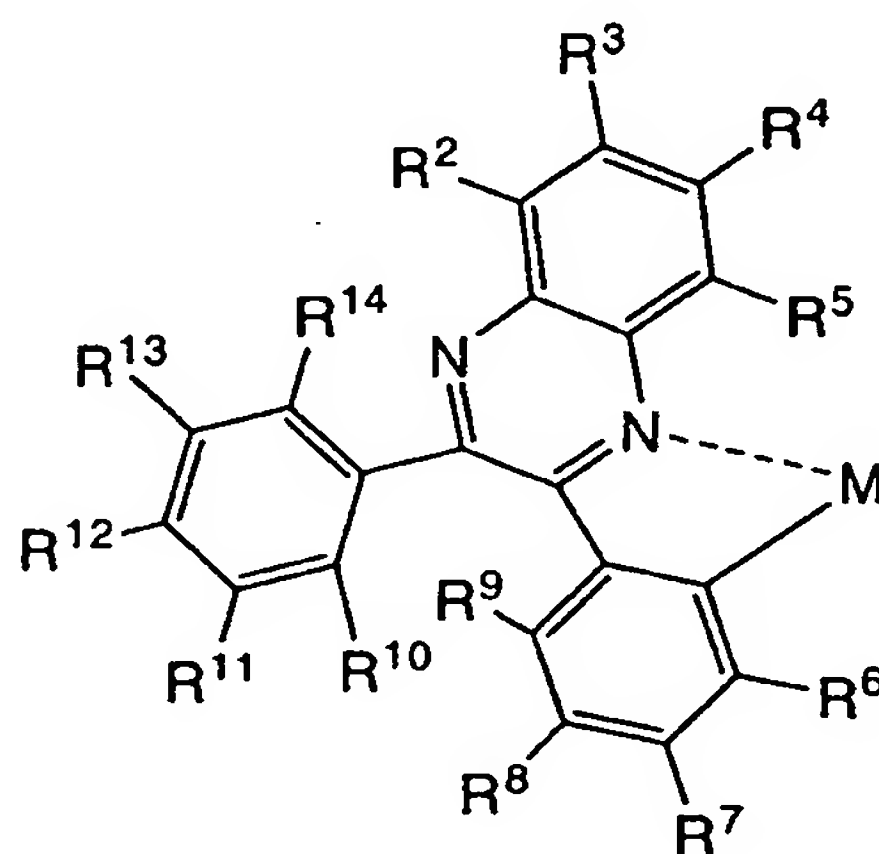
wherein each of R^1 to R^9 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10.

18. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (3) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

25

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(3)

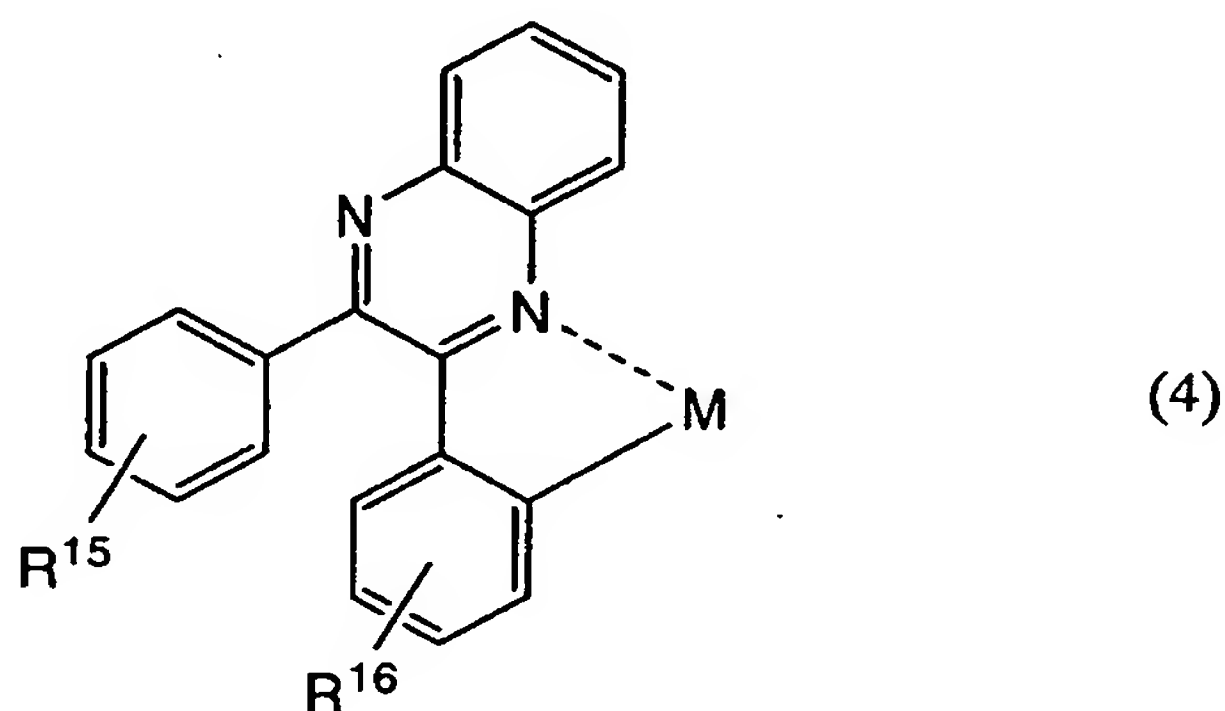
wherein each of R^2 to R^{14} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10.

5

19. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex having a structure represented by the following general formula (4) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

15



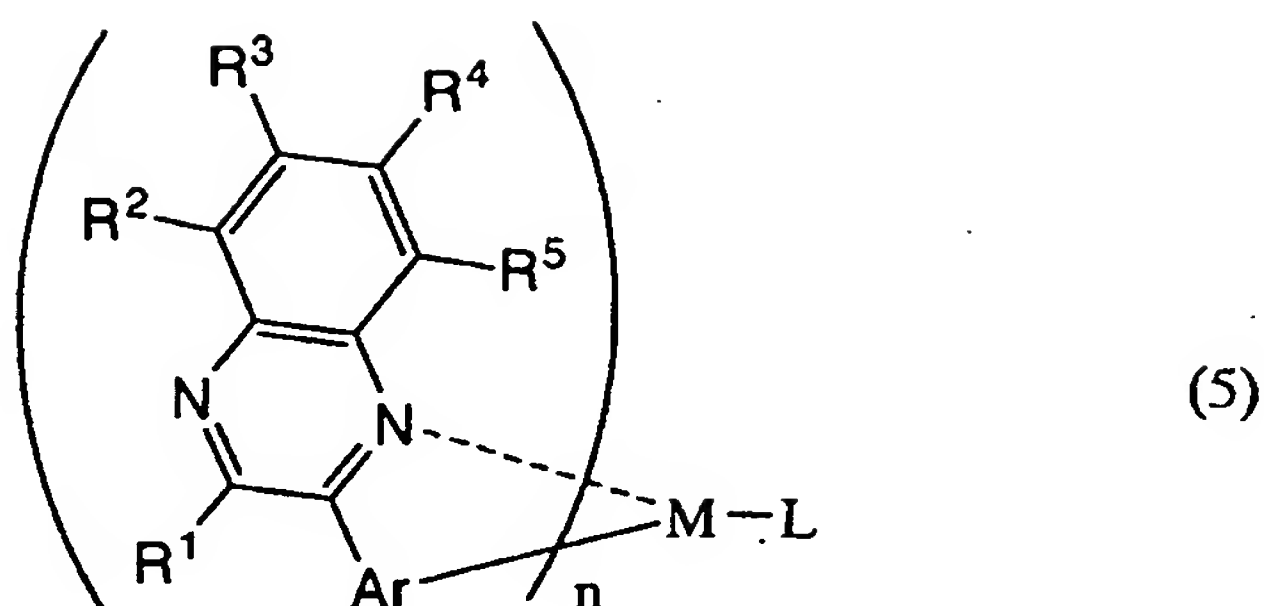
wherein each of R^{15} and R^{16} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxy group, an aryl group, a cyano group, and a heterocyclic group, and M is one of an element of Group 9 and an element of Group 10.

20. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (5) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

30

5



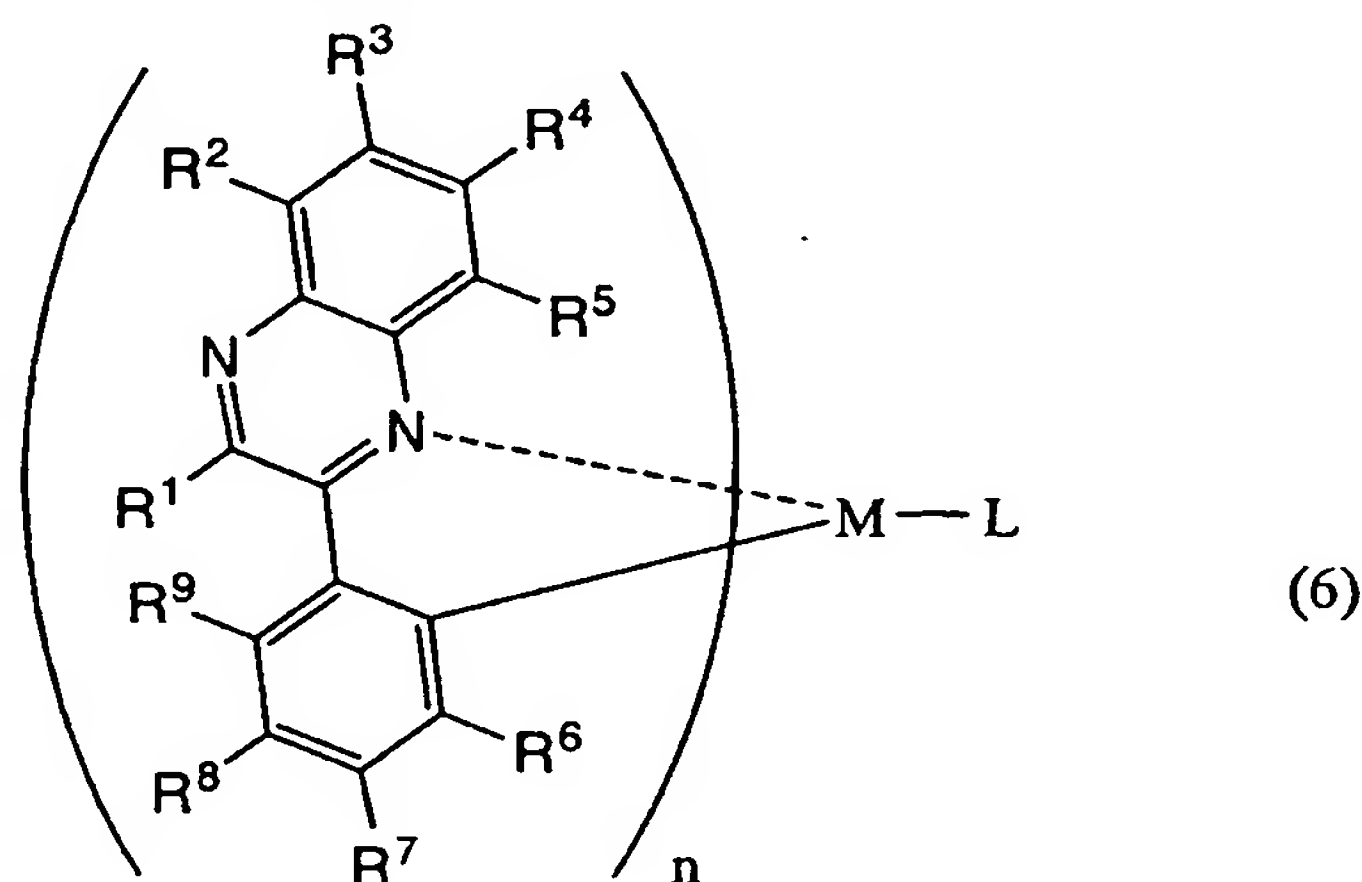
wherein each of R^1 to R^5 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, Ar is one of an aryl group having an electron-withdrawing group and a heterocyclic group having an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

21. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (6) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

20

25



wherein each of R^1 to R^9 is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a

cyano group, and a heterocyclic group, at least one of R^6 to R^9 is an electron-withdrawing group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

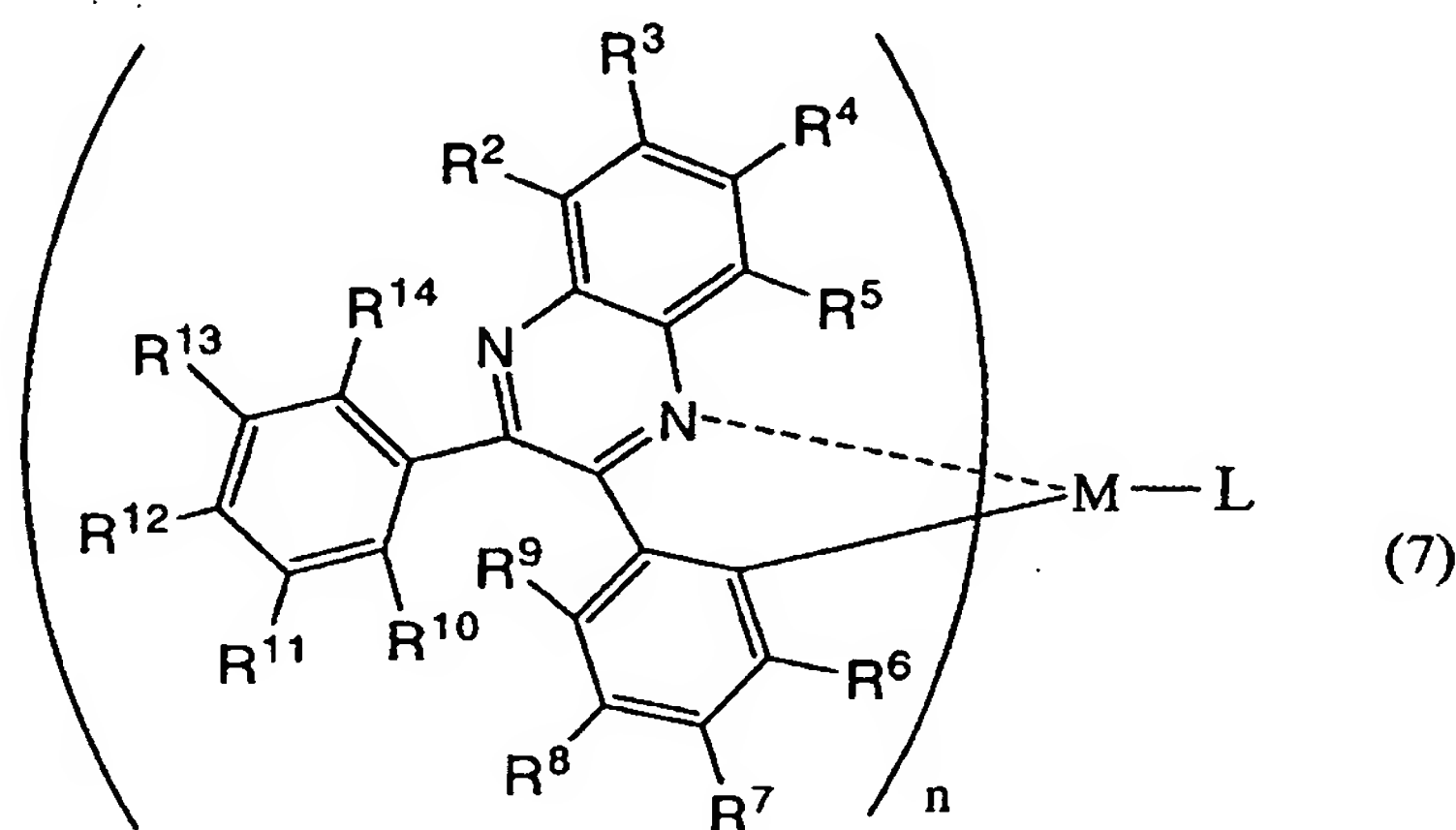
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22. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (7) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

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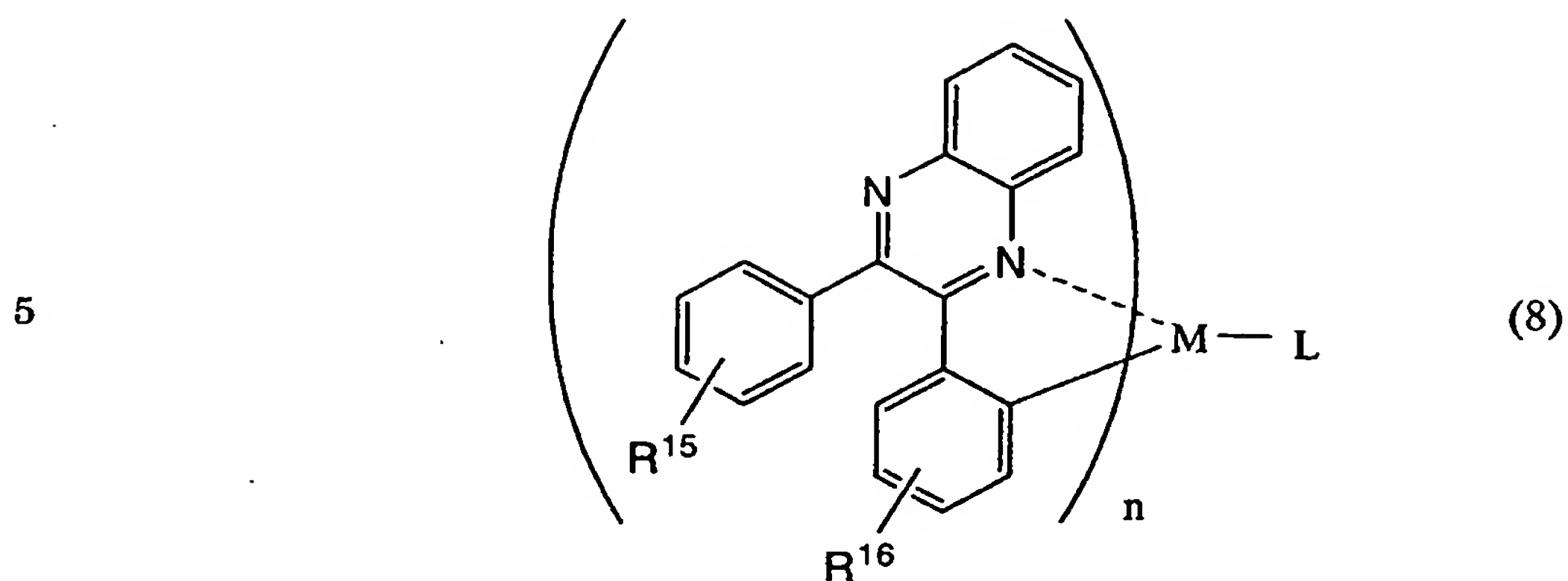
wherein each of R^2 to R^{14} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

25

23. A light-emitting element comprising a light-emitting layer between a pair of electrodes,

wherein the light-emitting layer comprises an organometallic complex represented by the following general formula (8) and a compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex, and

30



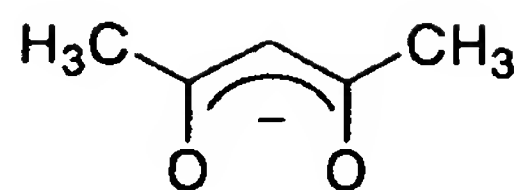
10 wherein each of R^{15} and R^{16} is selected from the group consisting of hydrogen, a halogen element, an acyl group, an alkyl group, an alkoxyl group, an aryl group, a cyano group, and a heterocyclic group, M is one of an element of Group 9 and an element of Group 10, $n = 2$ when the M is the element of Group 9 while $n = 1$ when the M is the element of Group 10, and L is an anionic ligand.

15 24. The light-emitting element according to any one of claims 20 to 23, wherein the anionic ligand L is one of an anionic ligand having a β -diketone structure, an anionic bidentate ligand having a carboxyl group, and a monoanionic bidentate ligand having a phenolic hydroxyl group.

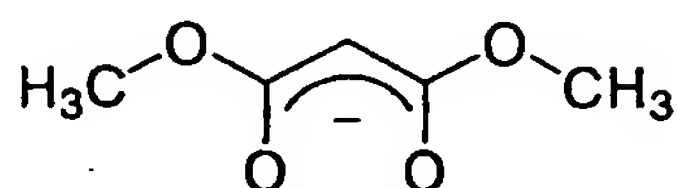
20 25. The light-emitting element according to any one of claims 20 to 23, wherein the anionic ligand L is a ligand represented by any one of the following formulas (9) to (15).

25

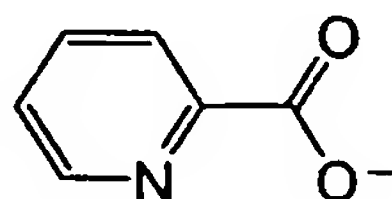
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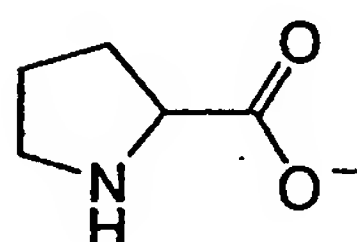
(9)



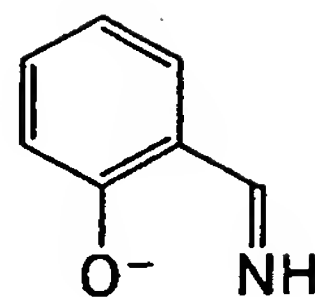
(10)



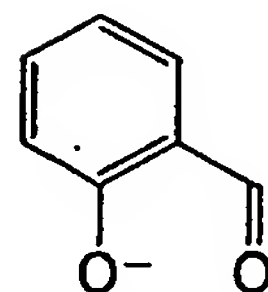
(11)



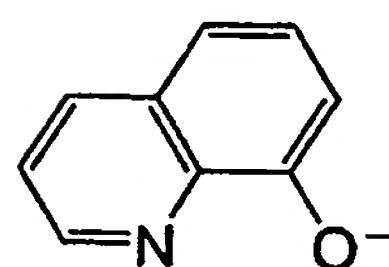
(12)



(13)



(14)



(15)

26. The light-emitting element according to any one of claims 16 to 23, wherein the light-emitting layer includes the organometallic complex and one of a first compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has an electron mobility of 10^{-6} cm²/Vs or more and a second compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or more.

27. The light-emitting element according to any one of claims 16 to 23, wherein the light-emitting layer includes the organometallic complex, a first compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has an electron mobility of 10^{-6} cm²/Vs or more, and a second compound that has a larger ionization potential and a smaller electron affinity than the organometallic complex and has a hole mobility of 10^{-6} cm²/Vs or more.

25

28. The light-emitting element according to claim 26, wherein the first compound is a metal complex, and the second compound is an aromatic amine compound.

30

29. The light-emitting element according to claim 27, wherein the first

compound is a metal complex, and the second compound is an aromatic amine compound.

30. The light-emitting element according to any one of claims 1 to 8, further
5 comprising at least one of a hole injecting layer, a hole transporting layer, a hole blocking layer, an electron transporting layer, and an electron injecting layer.

31. The light-emitting element according to any one of claims 16 to 23, further
10 comprising at least one of a hole injecting layer, a hole transporting layer, a hole blocking layer, an electron transporting layer, and an electron injecting layer.

32. A light-emitting device using the light-emitting element according to any one of claims 1 to 8.

15 33. A light-emitting device using the light-emitting element according to any one of claims 16 to 23.

FIG. 1

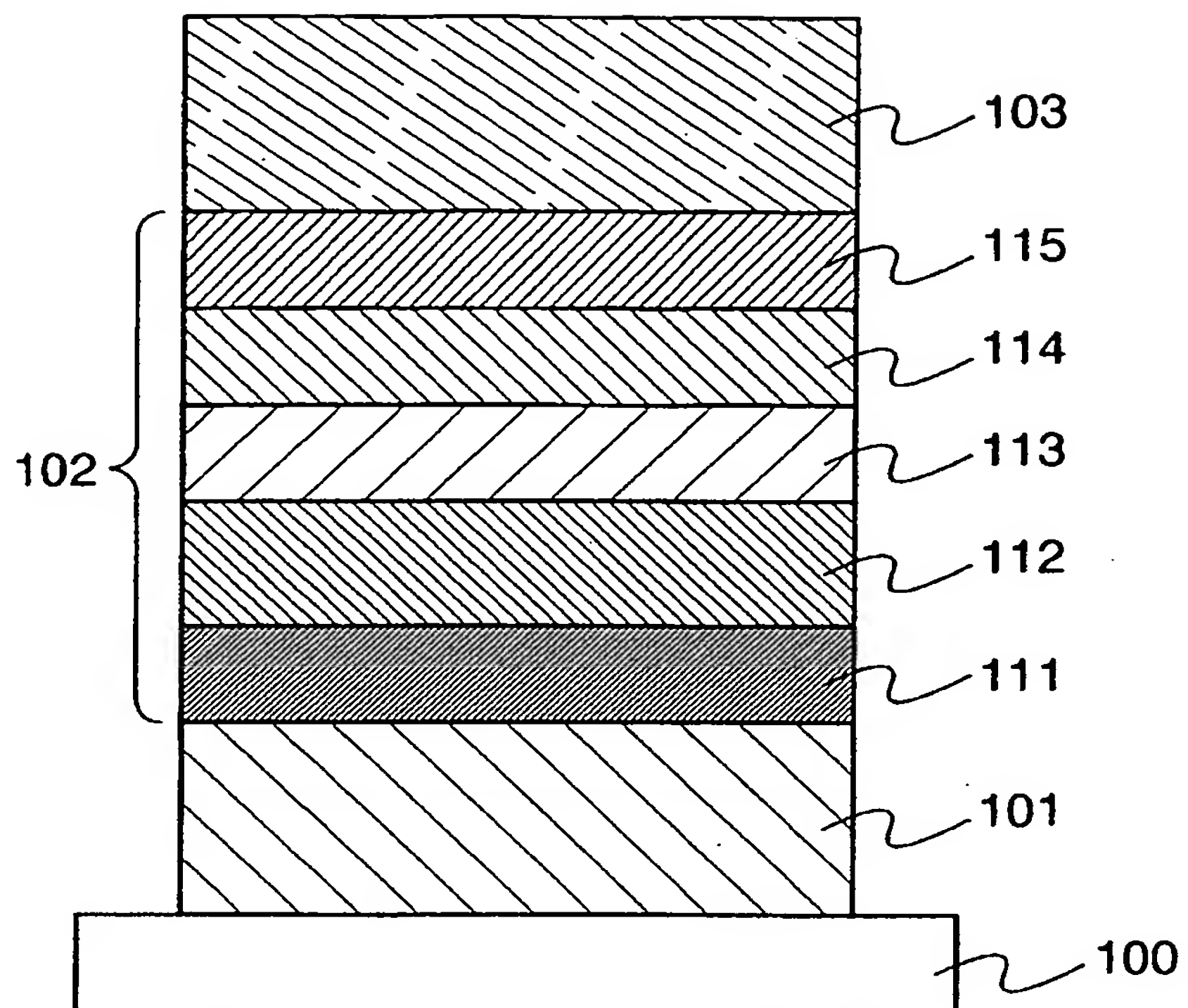


FIG. 2

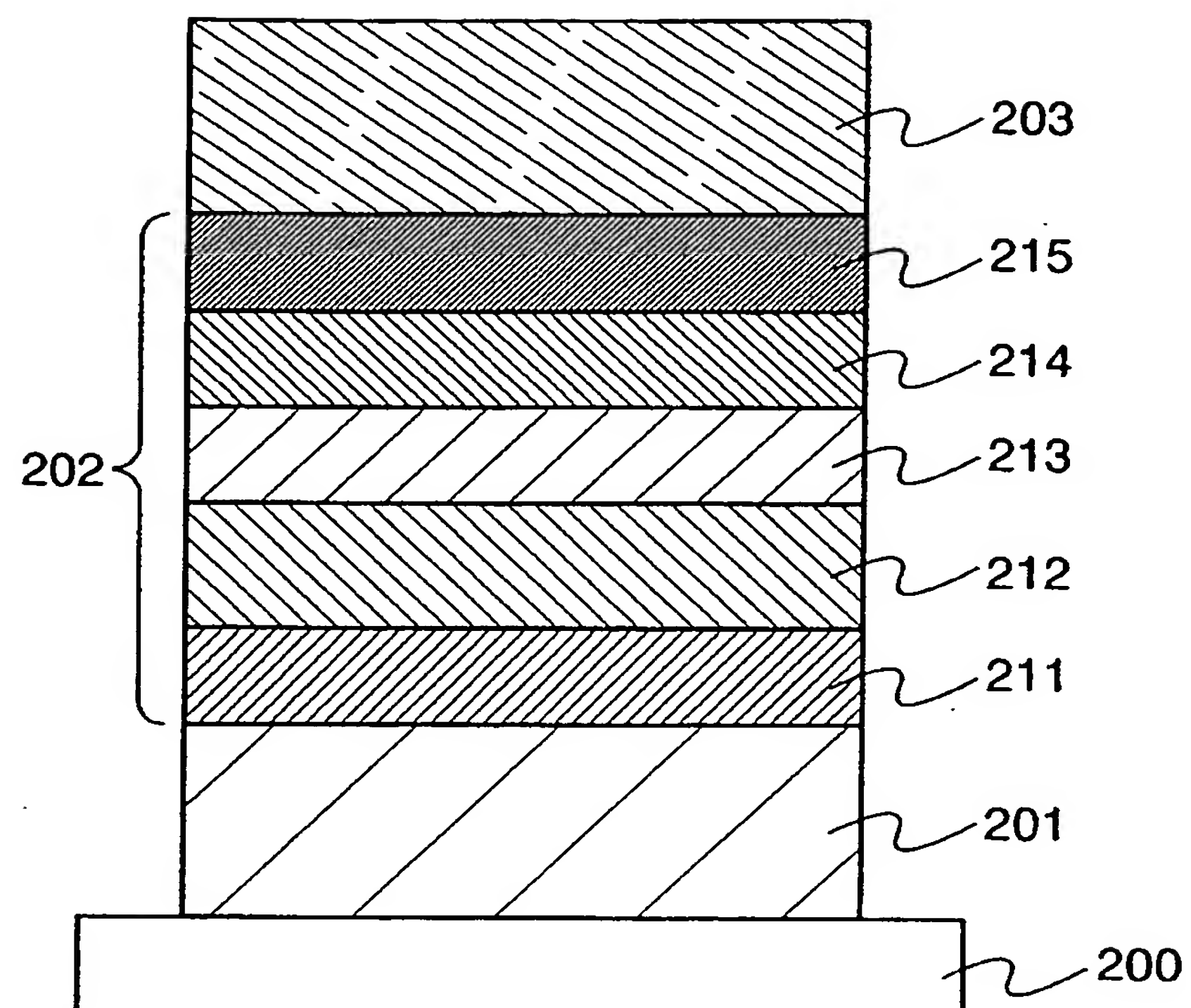


FIG. 3

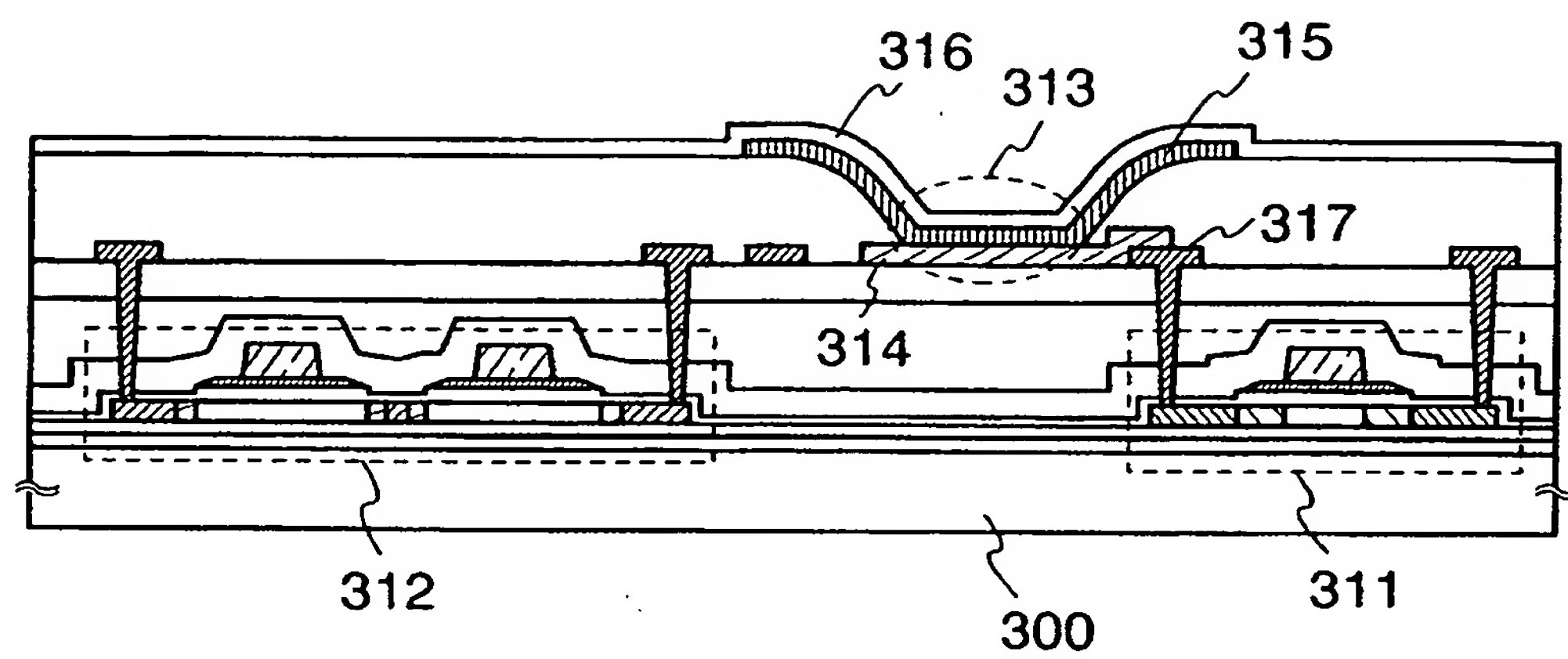


FIG. 4

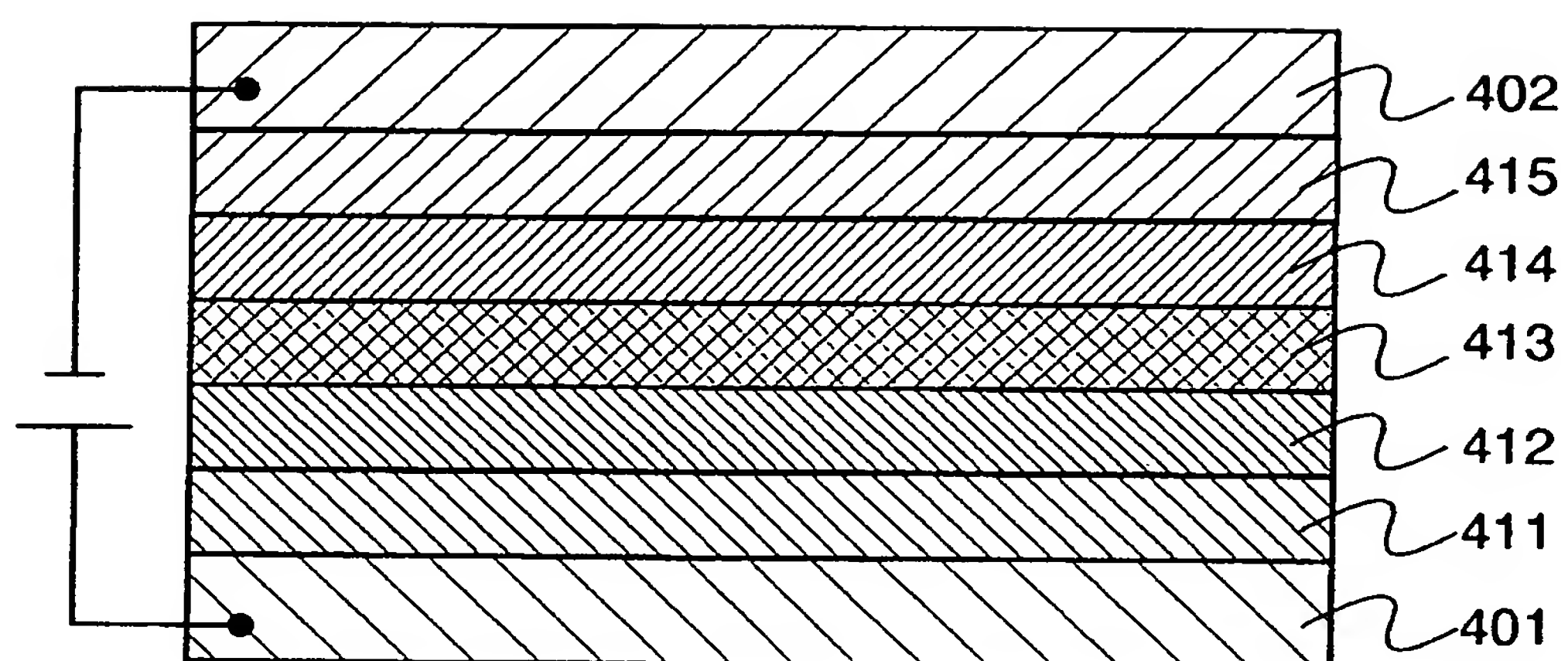


FIG. 5

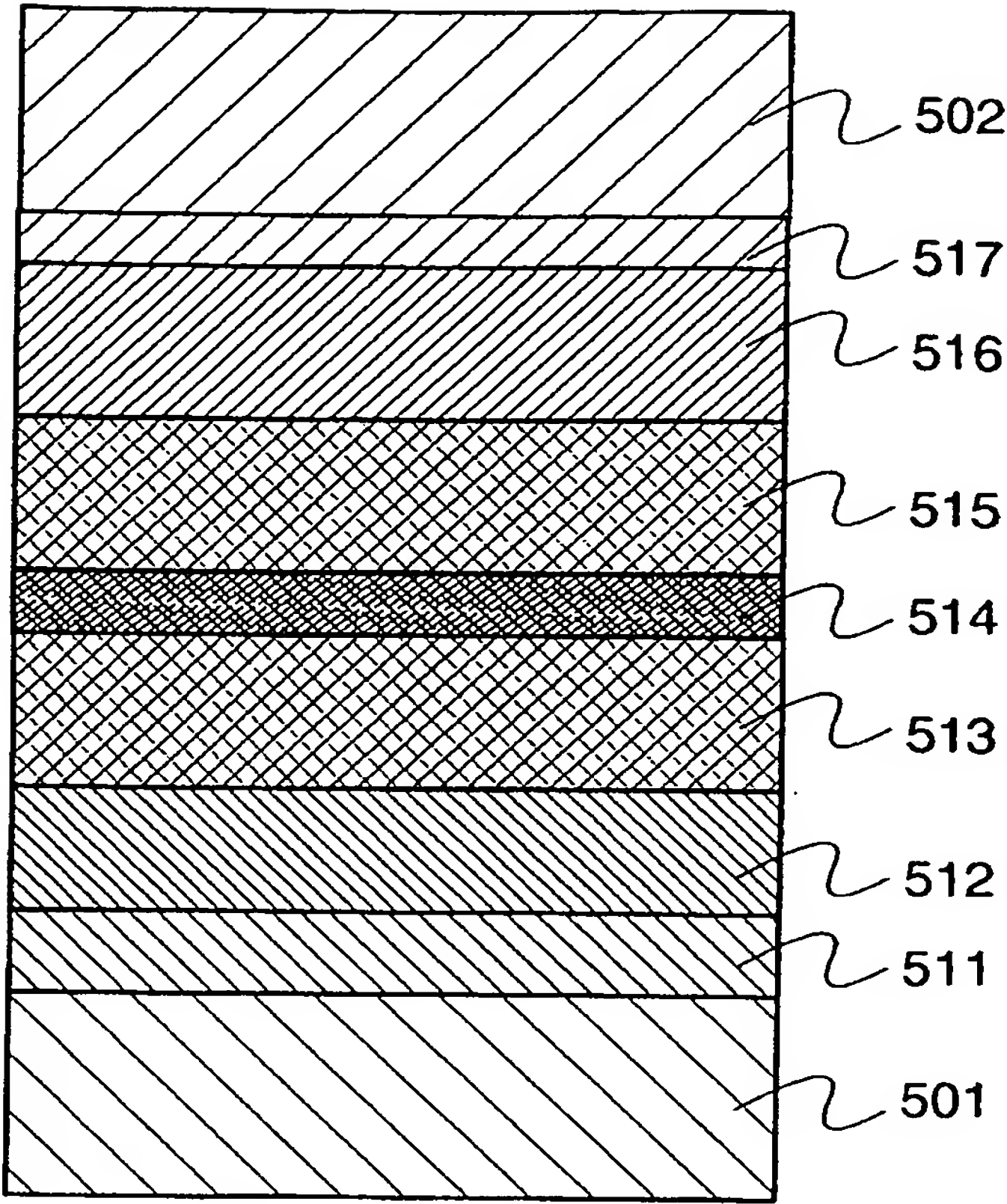


FIG. 6

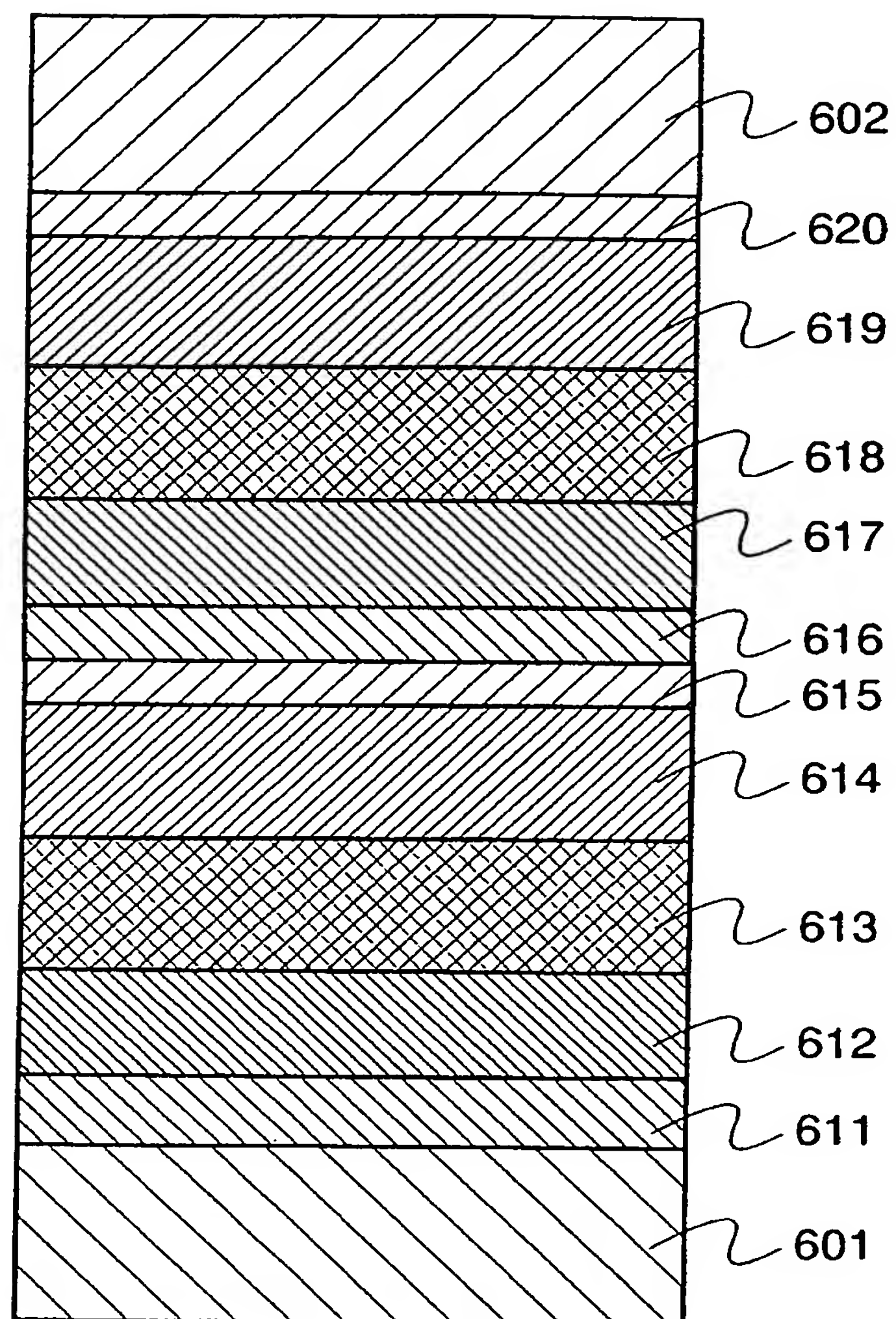


FIG. 7

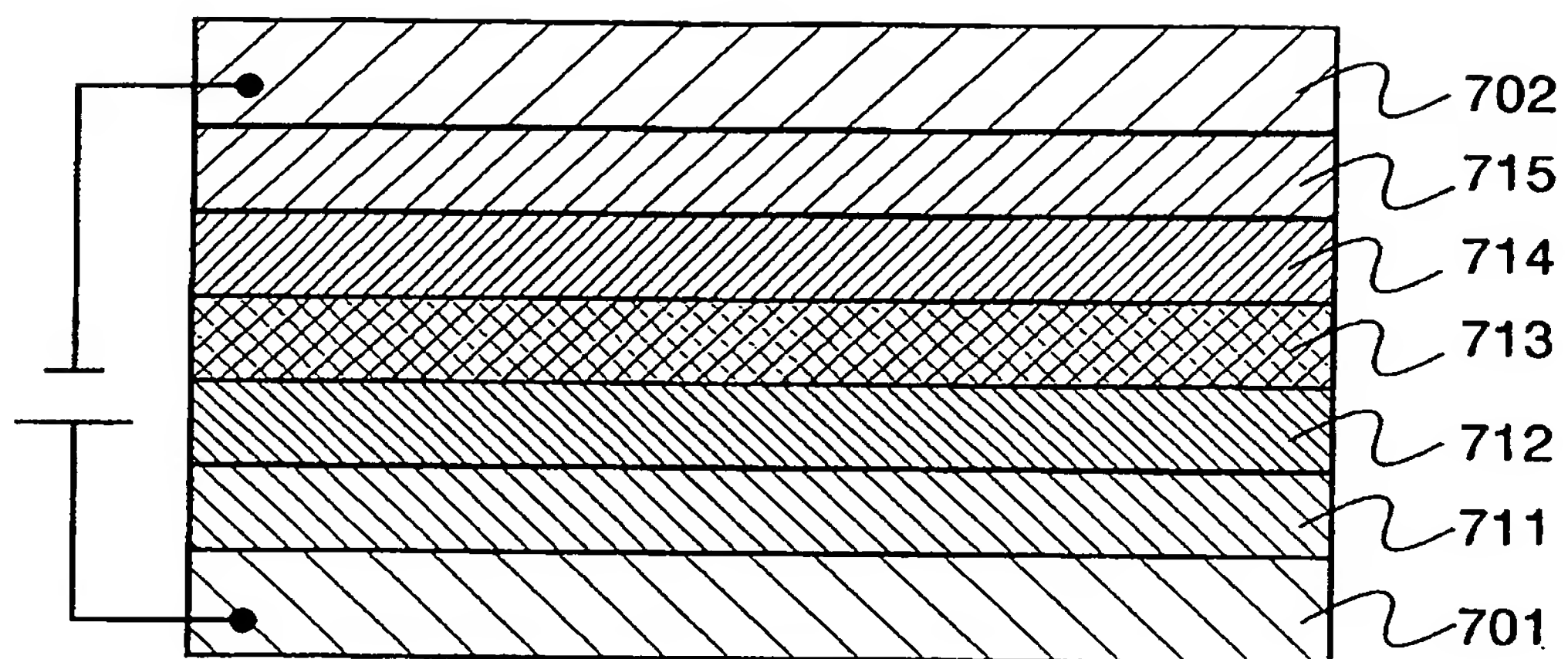
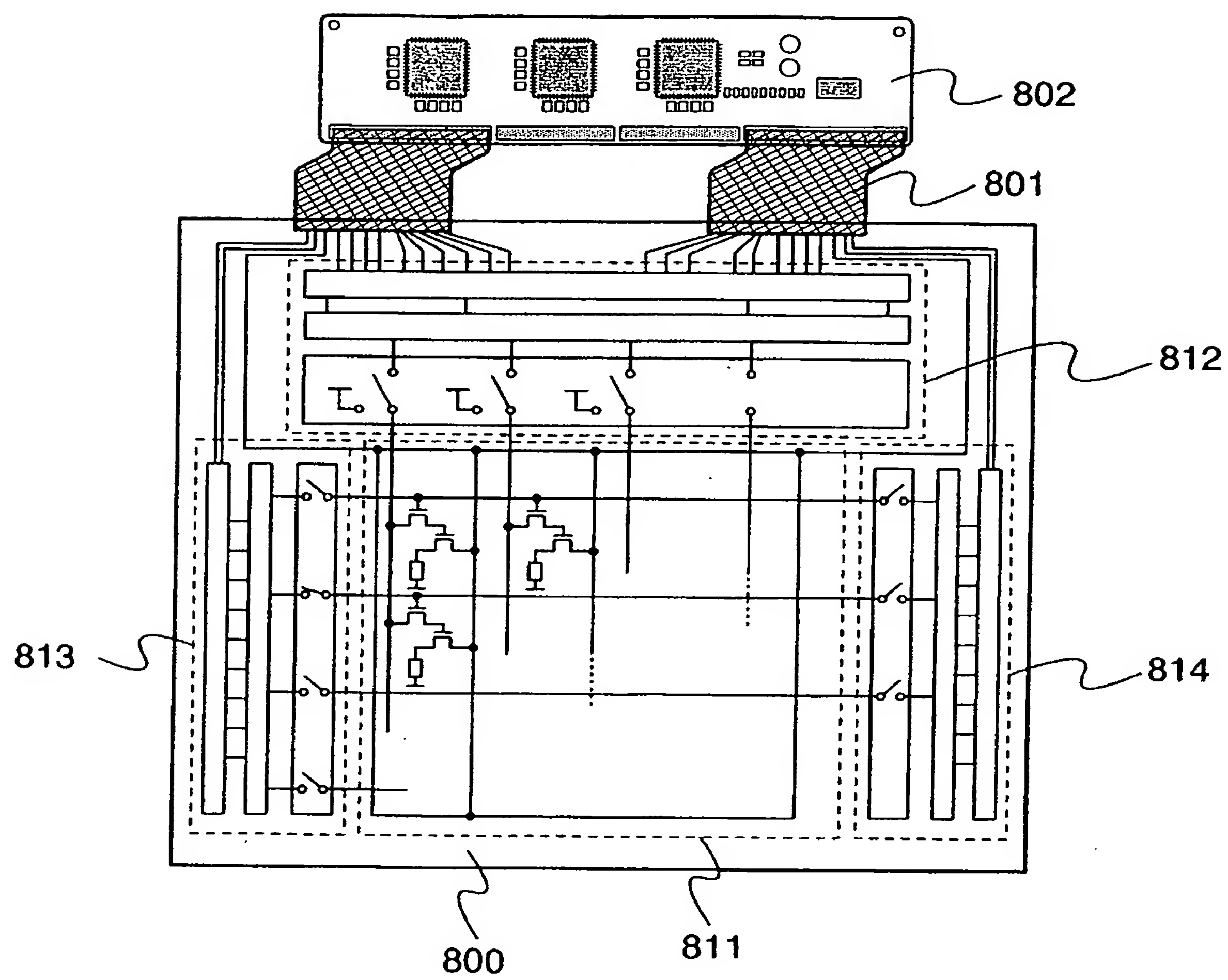


FIG. 8



9/48

FIG. 9

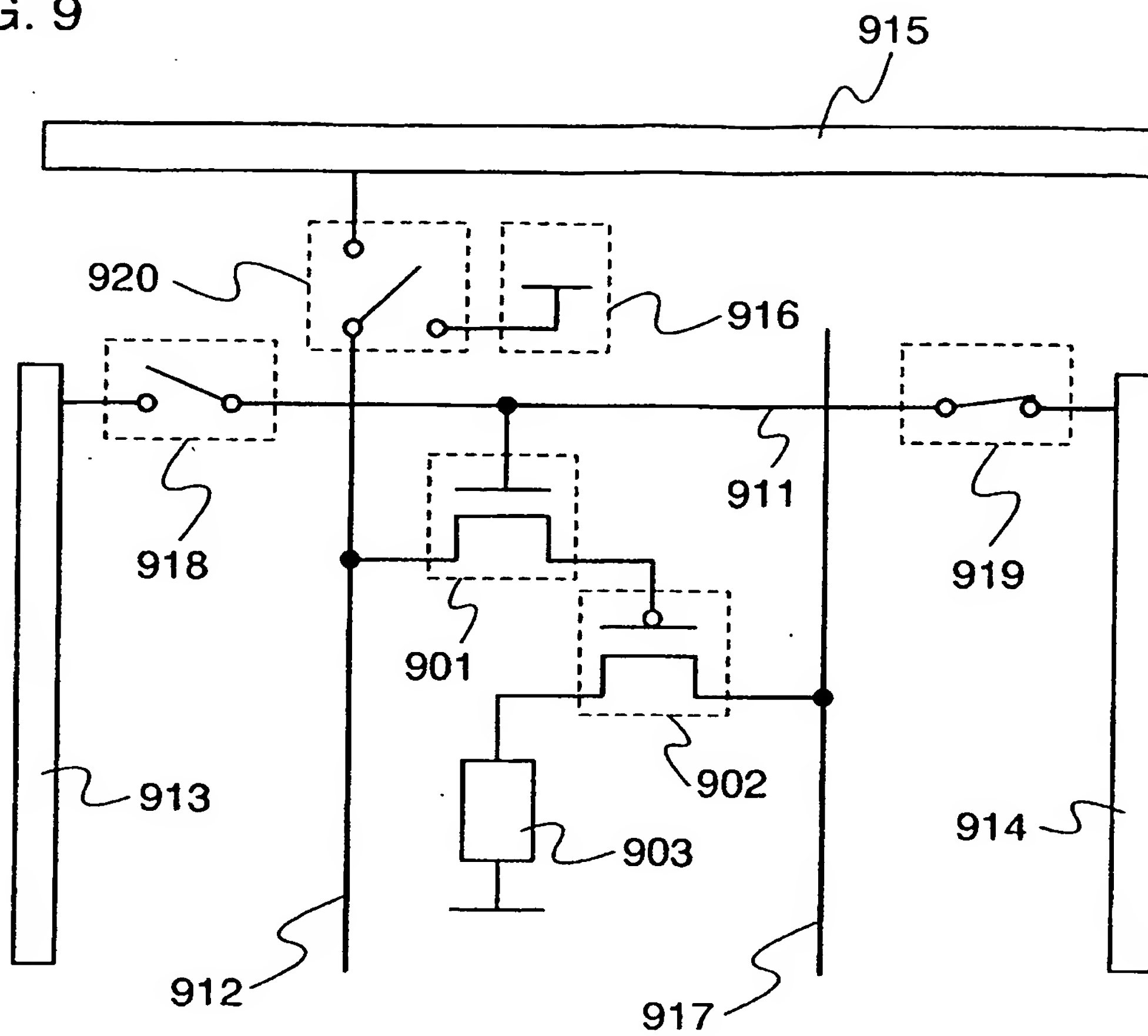


FIG. 10

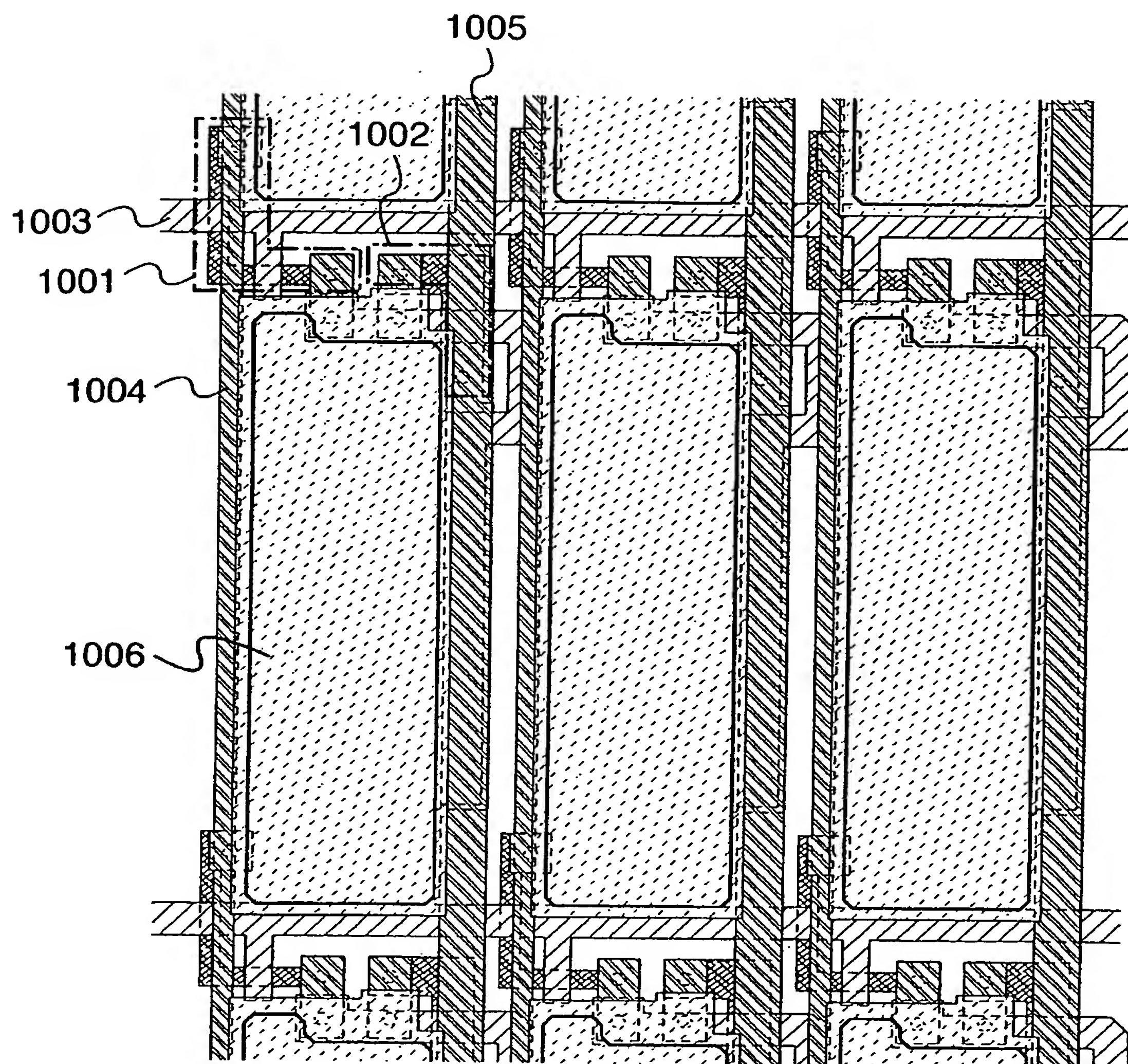


FIG. 11

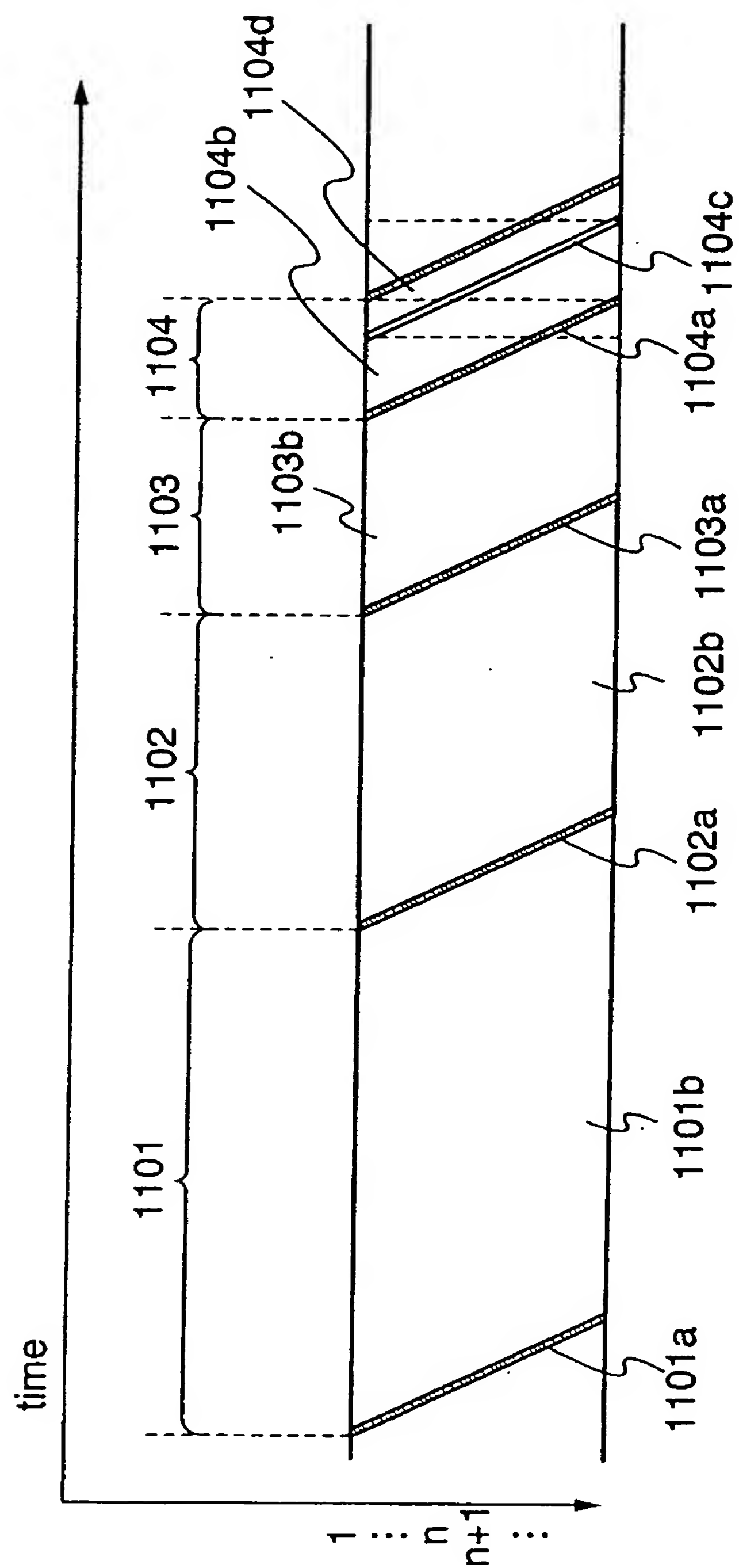


FIG. 12A

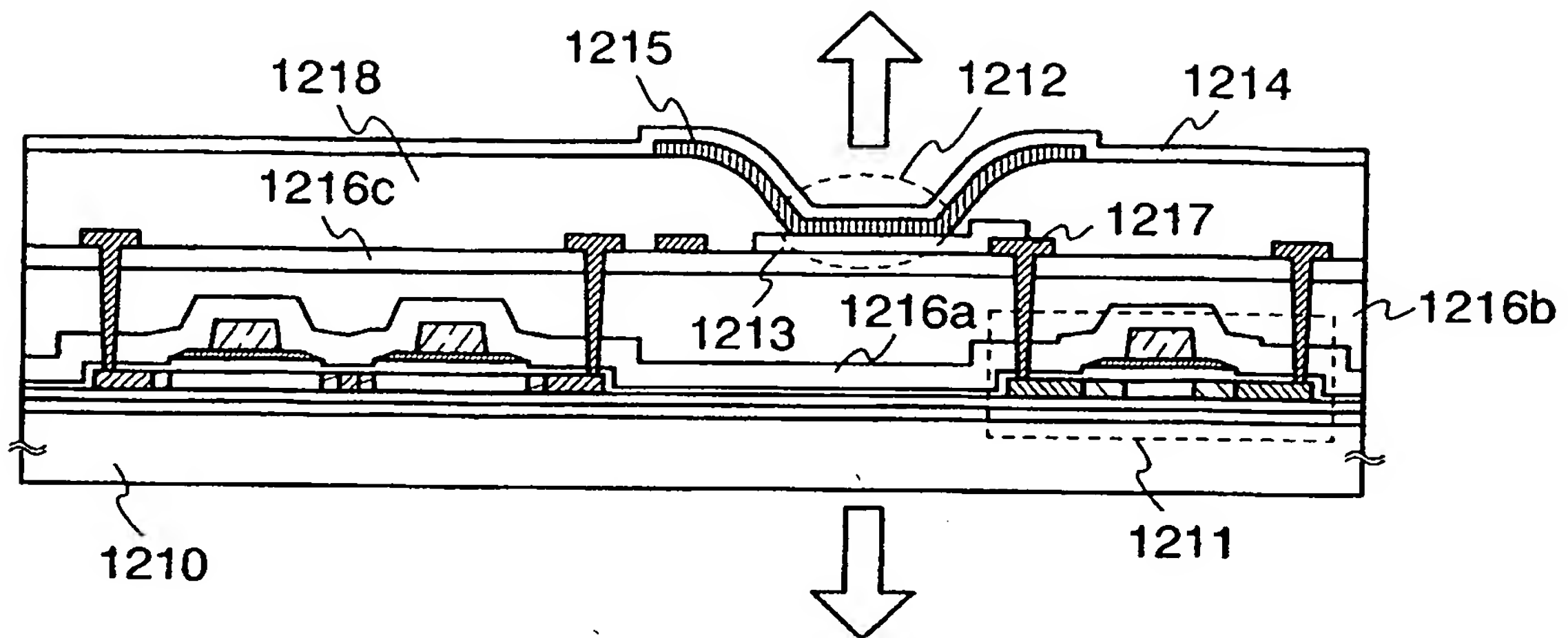


FIG. 12B

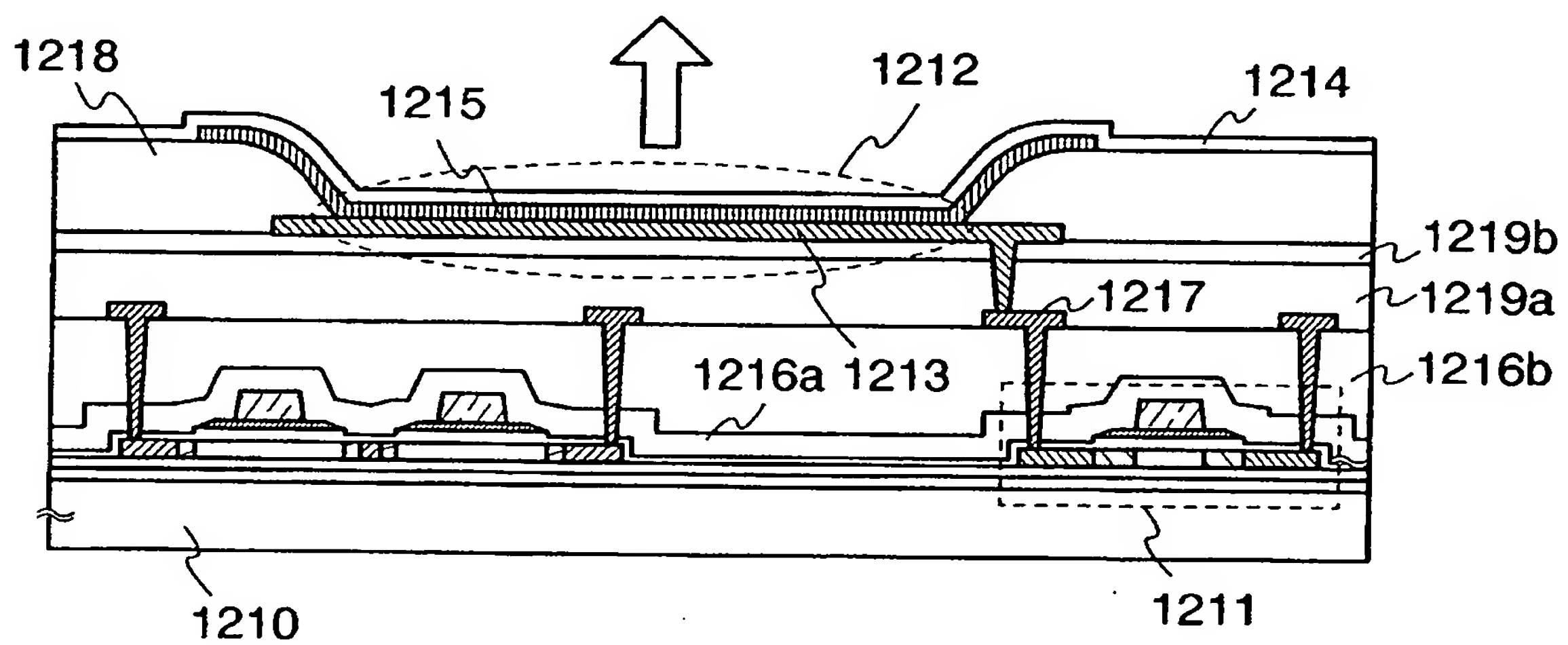
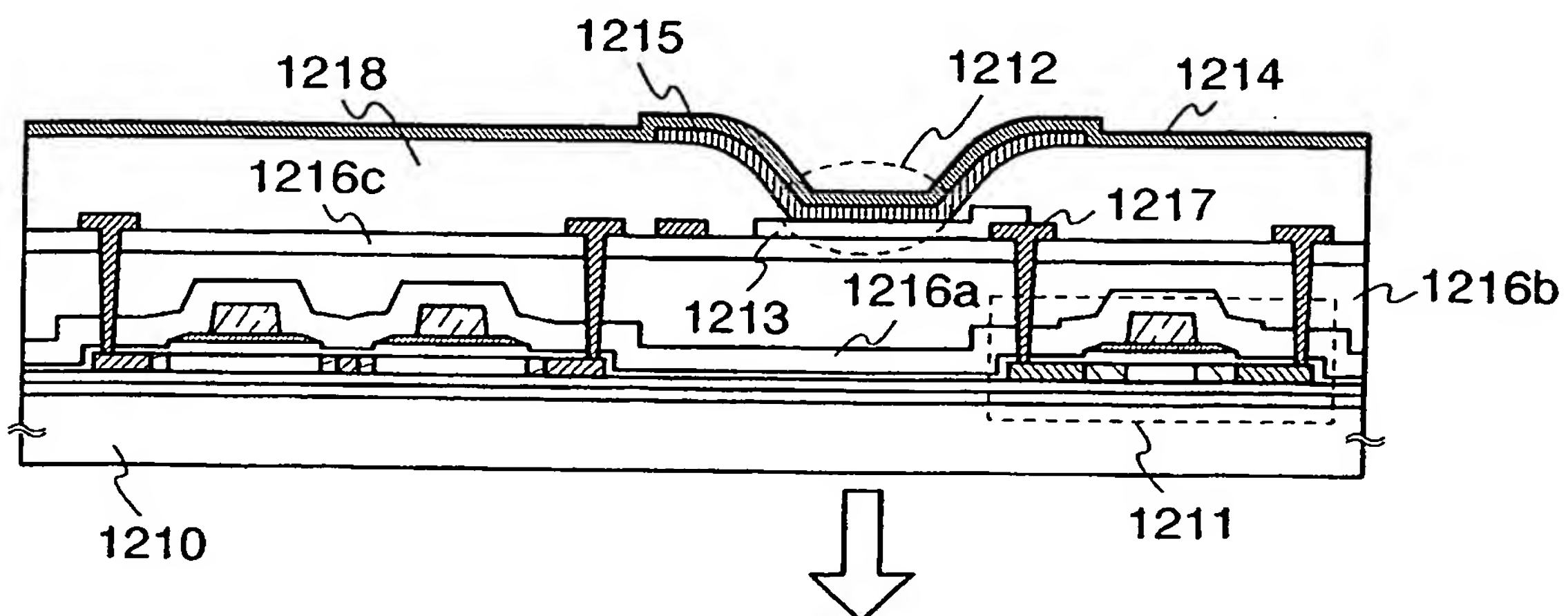
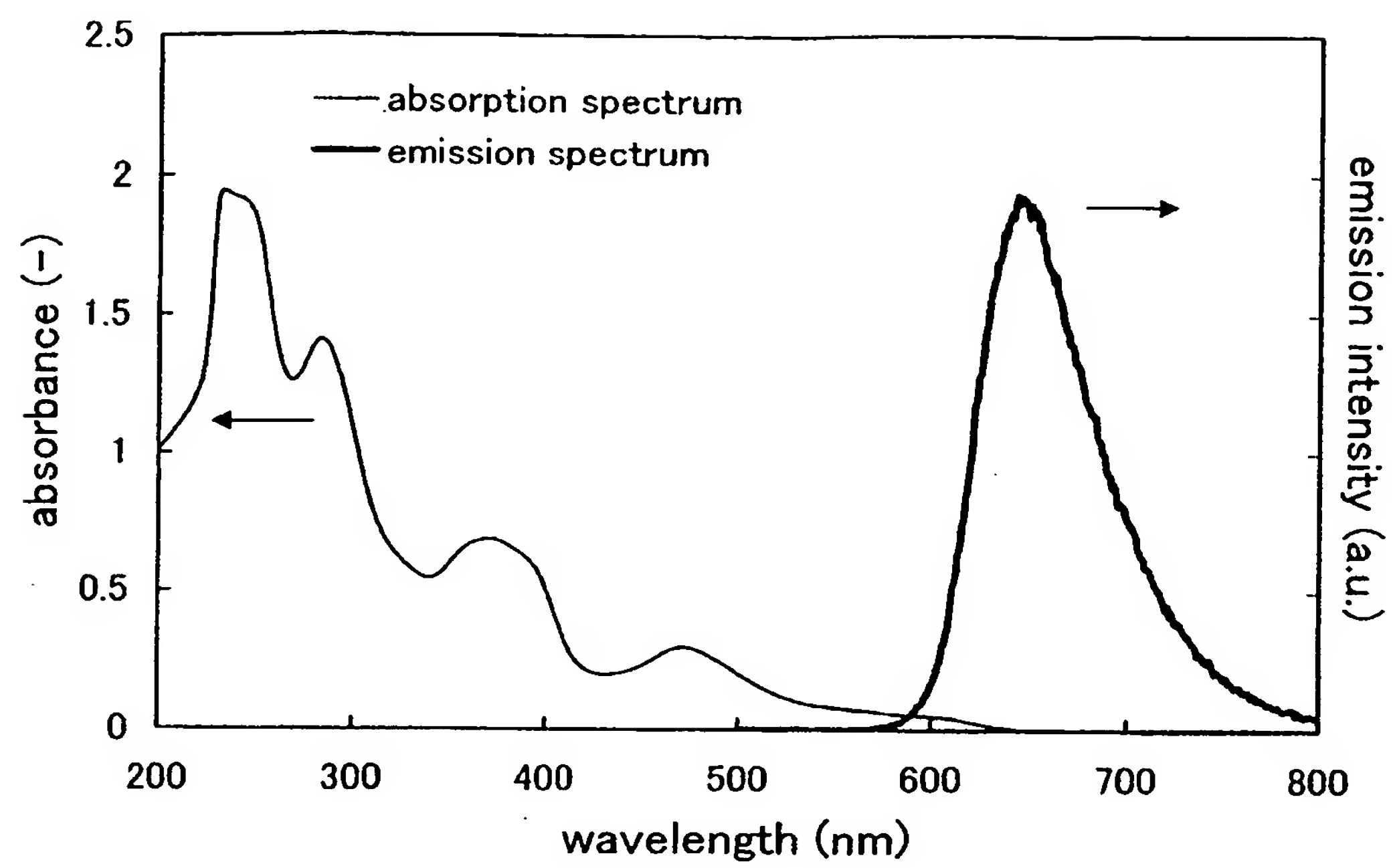


FIG. 12C



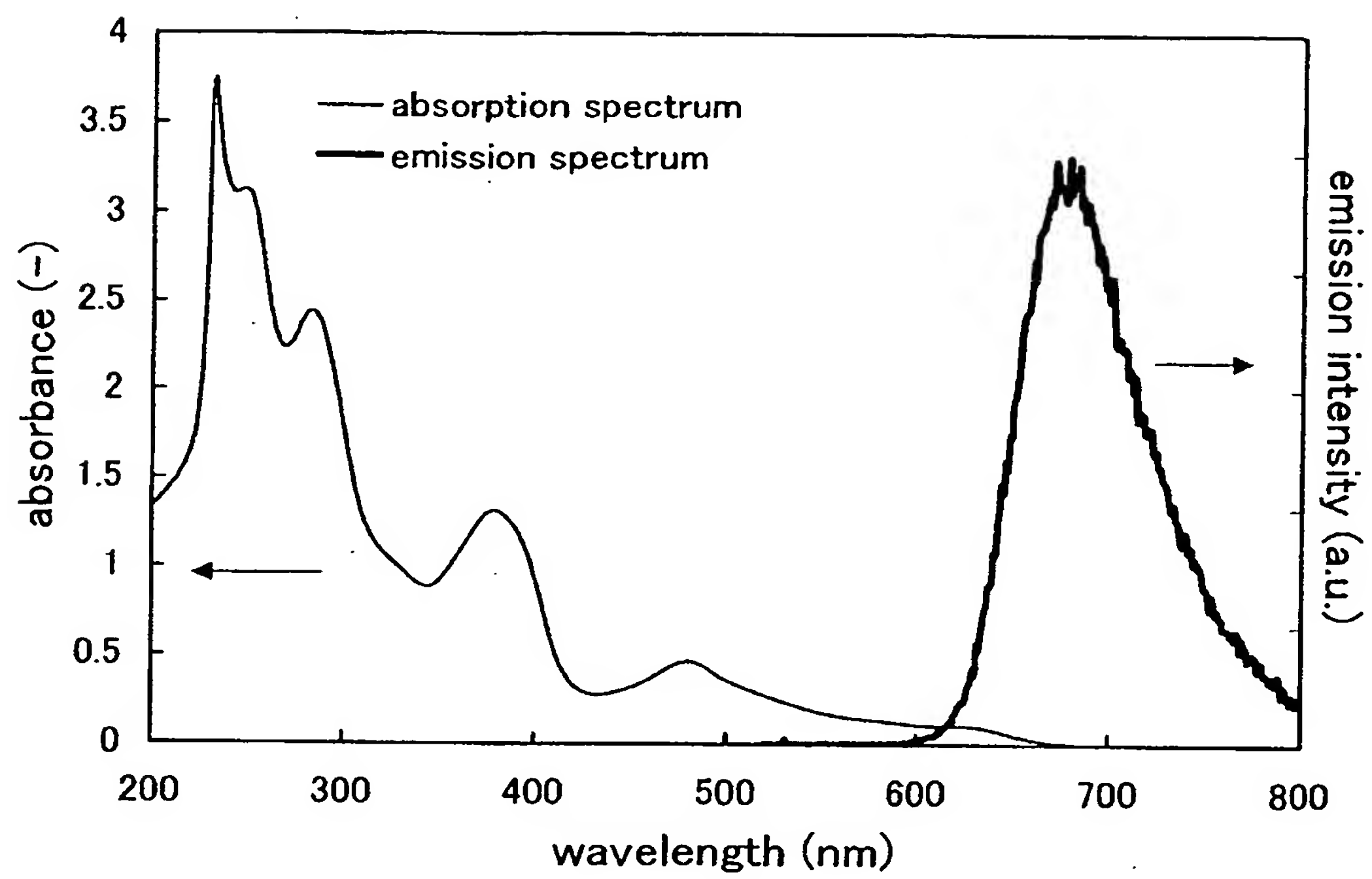
13/48

FIG. 13



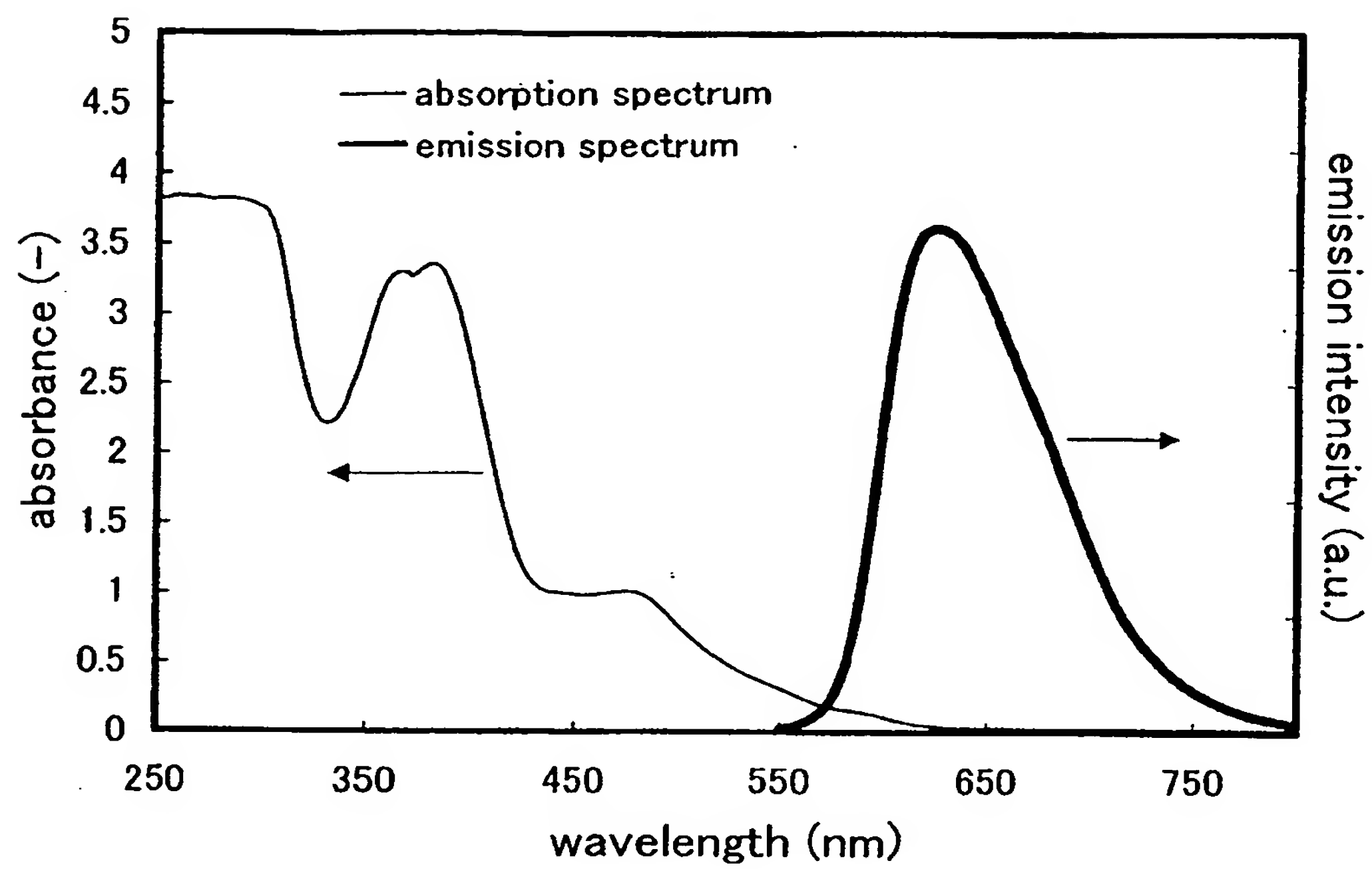
14/48

FIG. 14



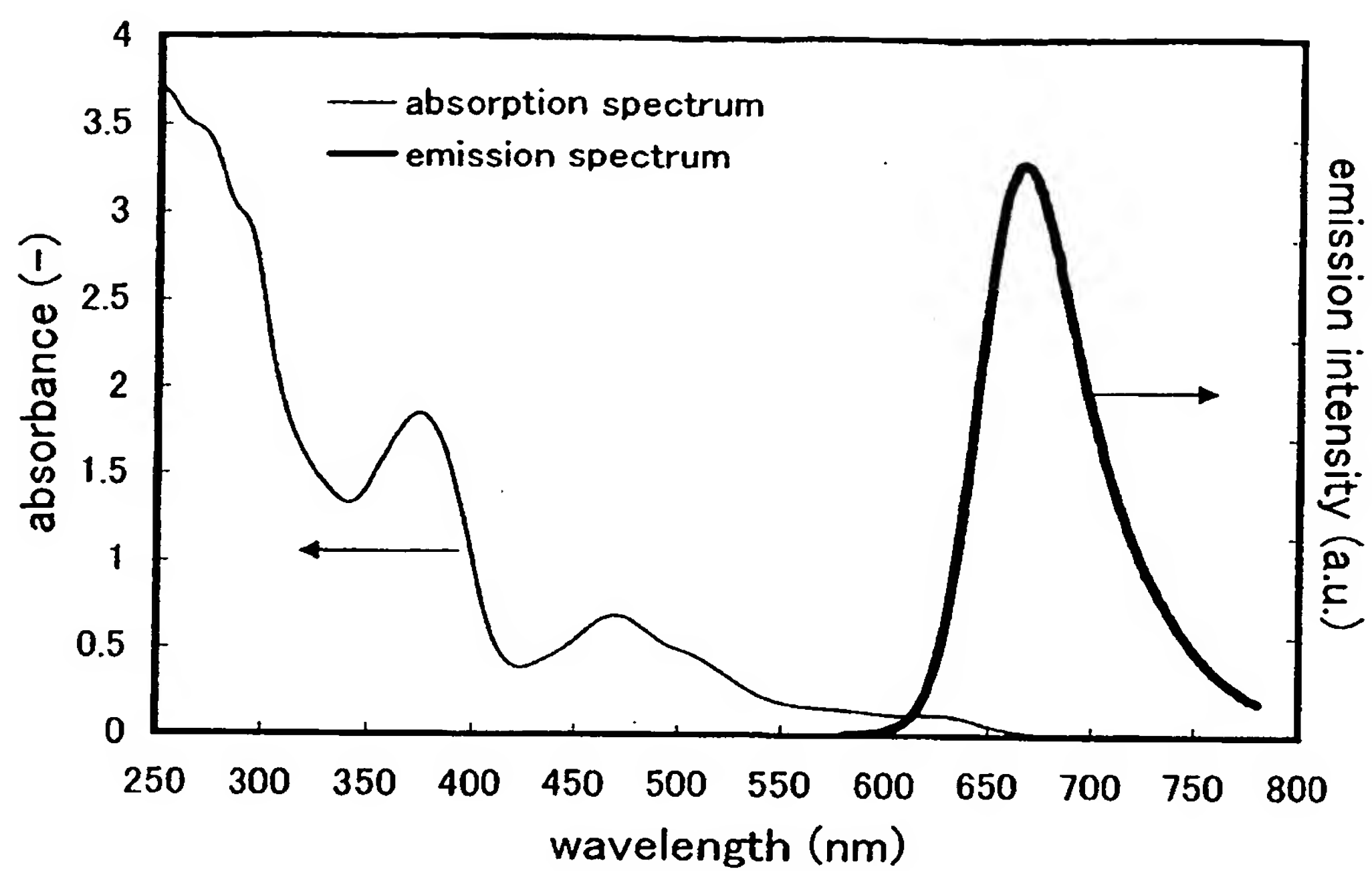
15/48

FIG. 15



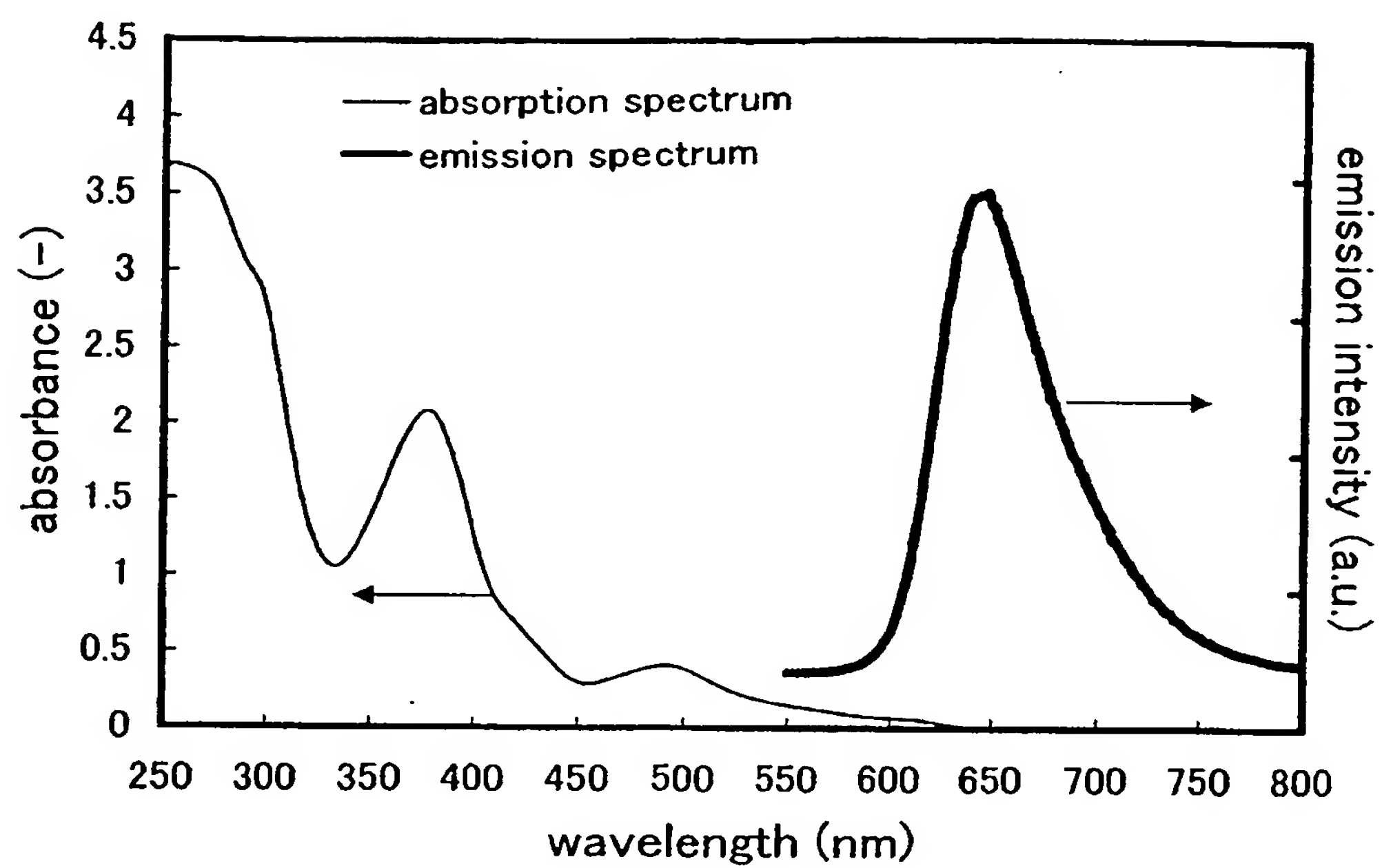
16/48

FIG. 16



17/48

FIG. 17



18/48

FIG. 18A

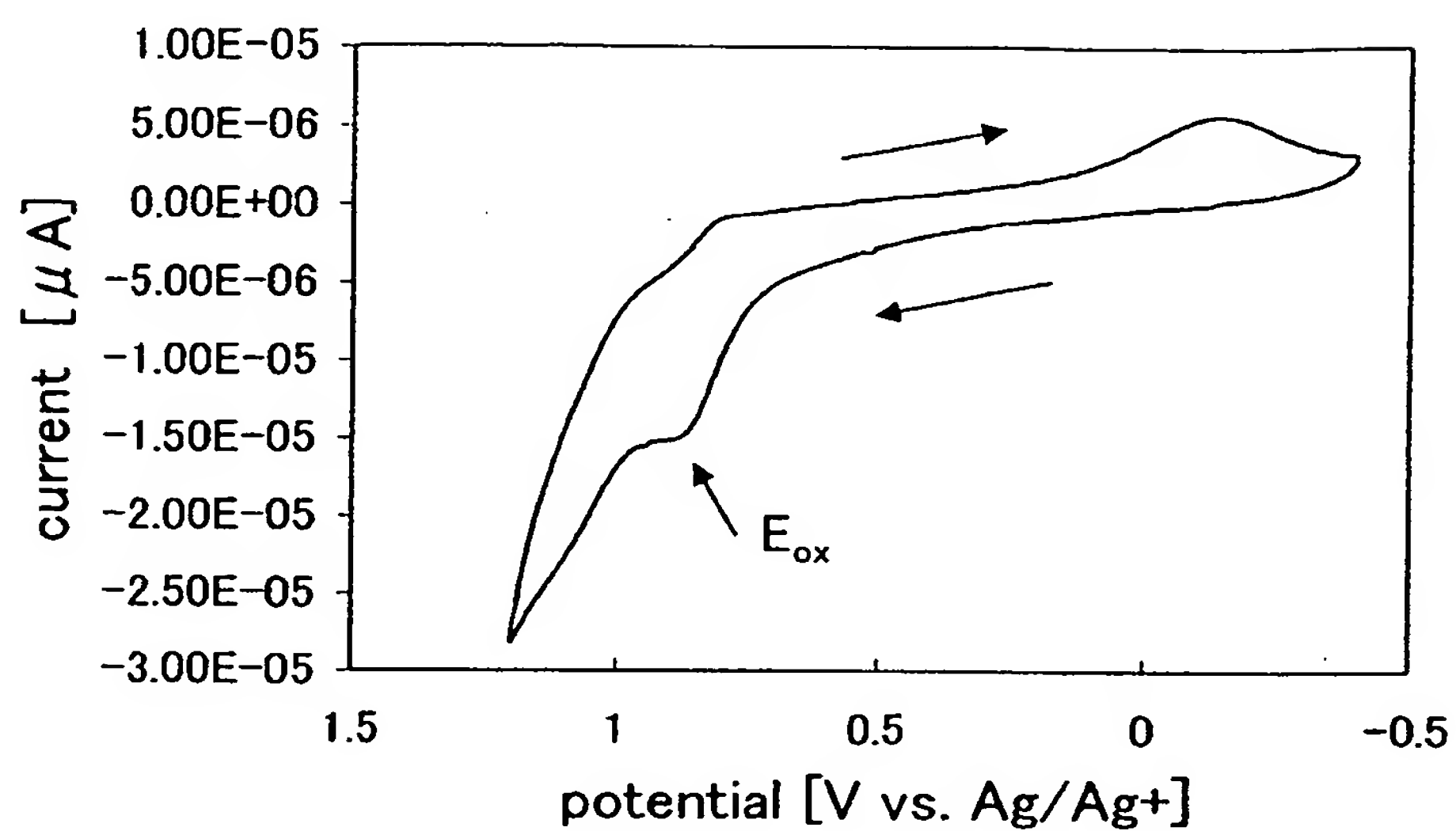


FIG. 18B

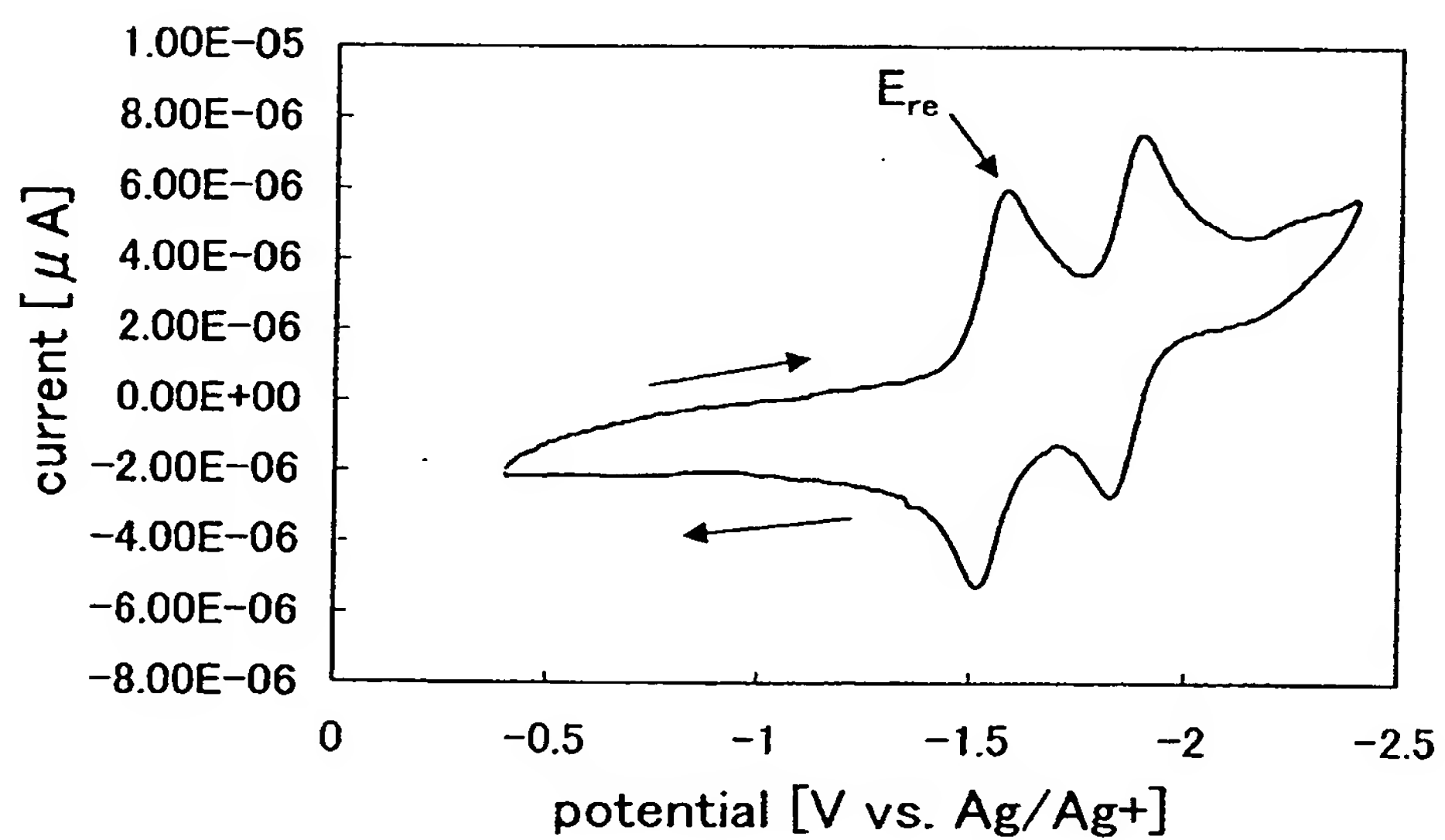
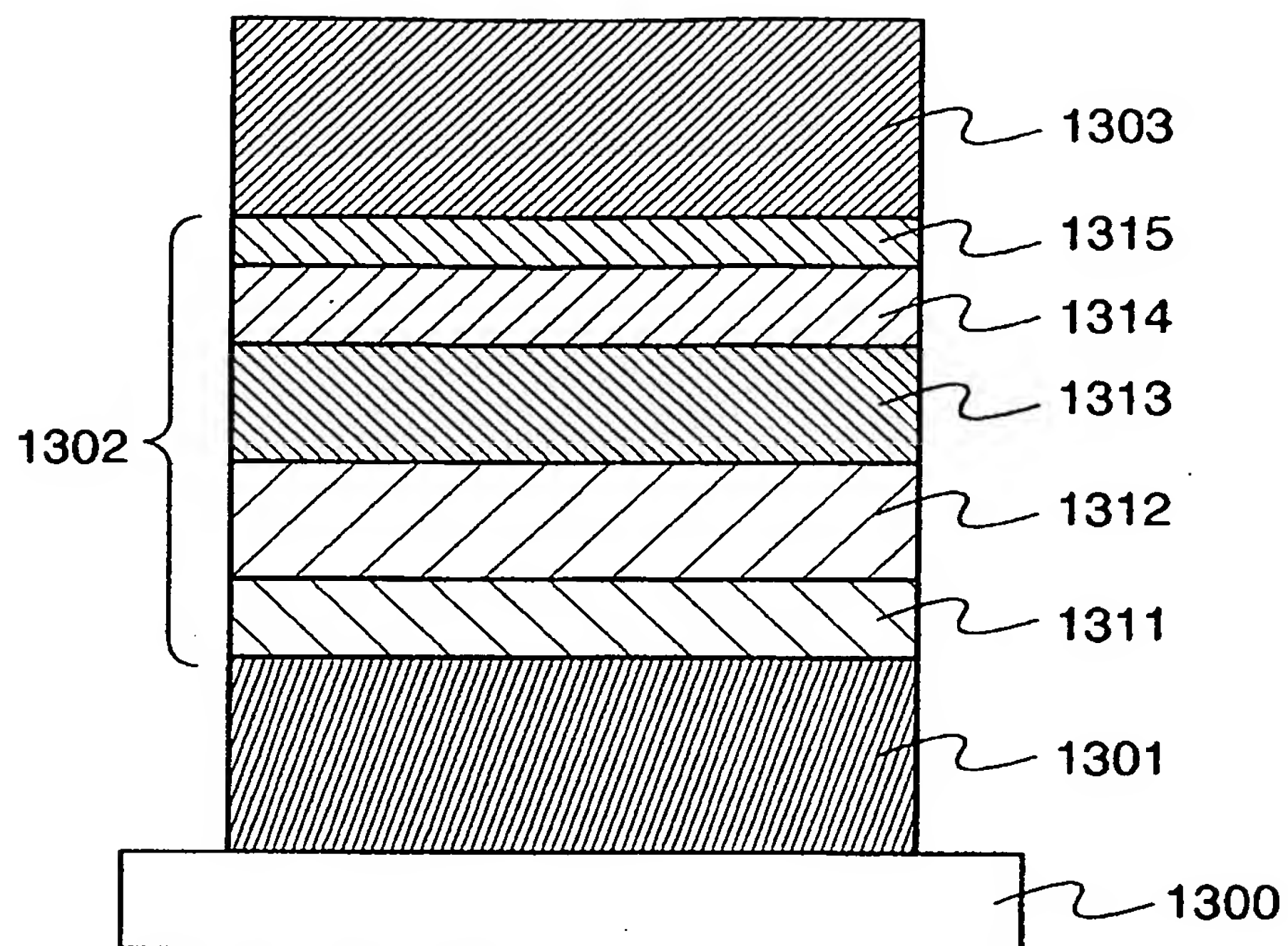


FIG. 19



20/48

FIG. 20A

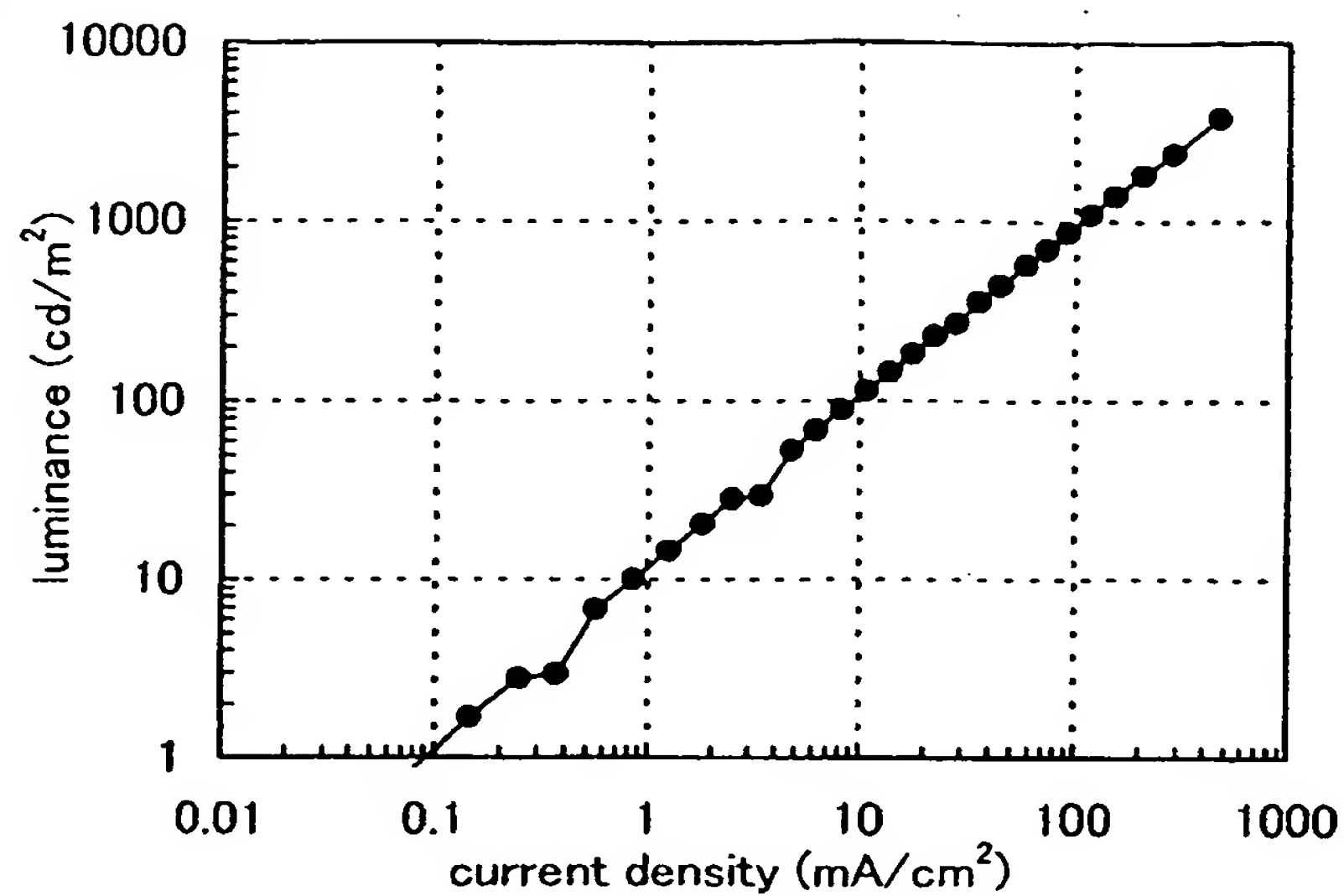


FIG. 20B

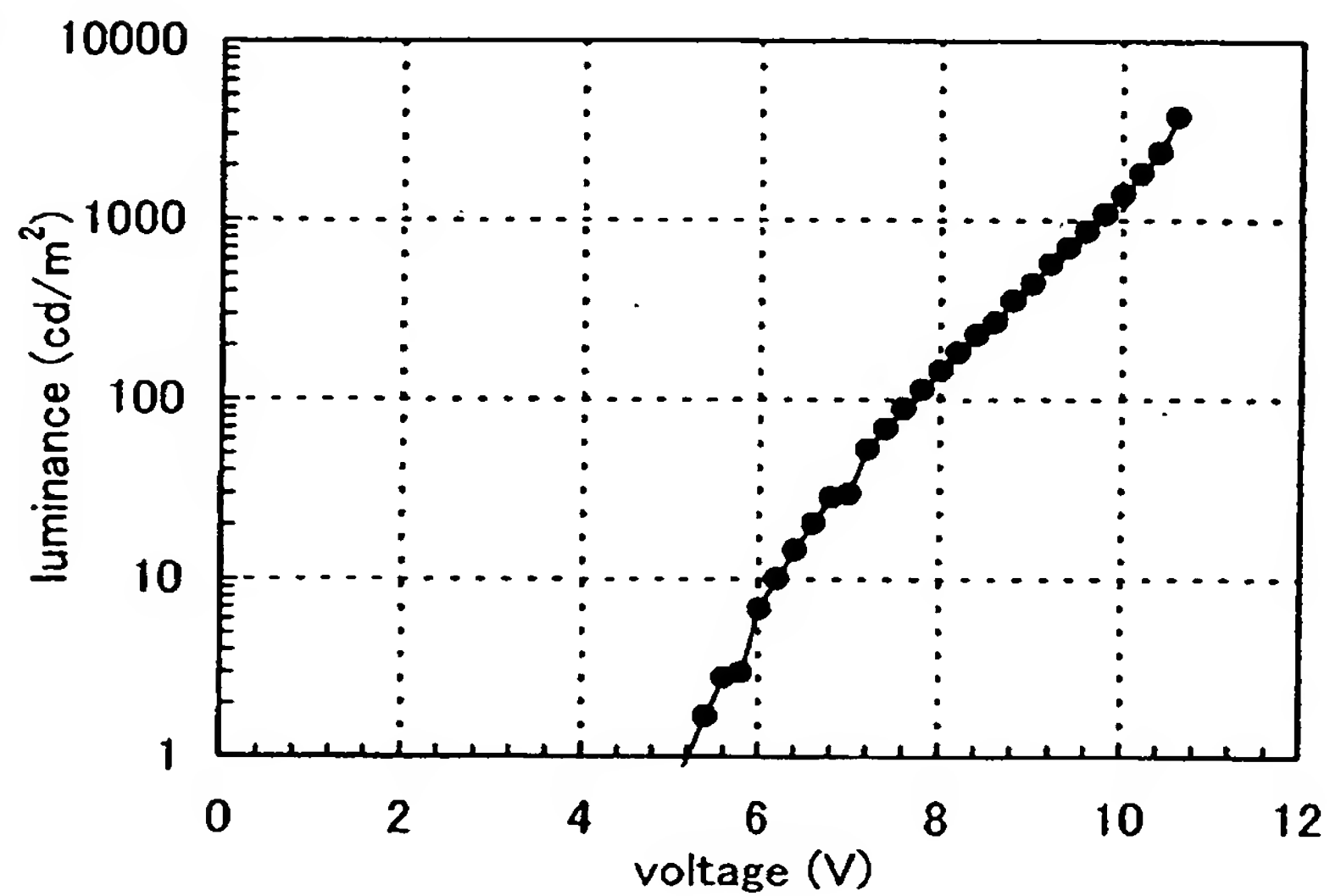
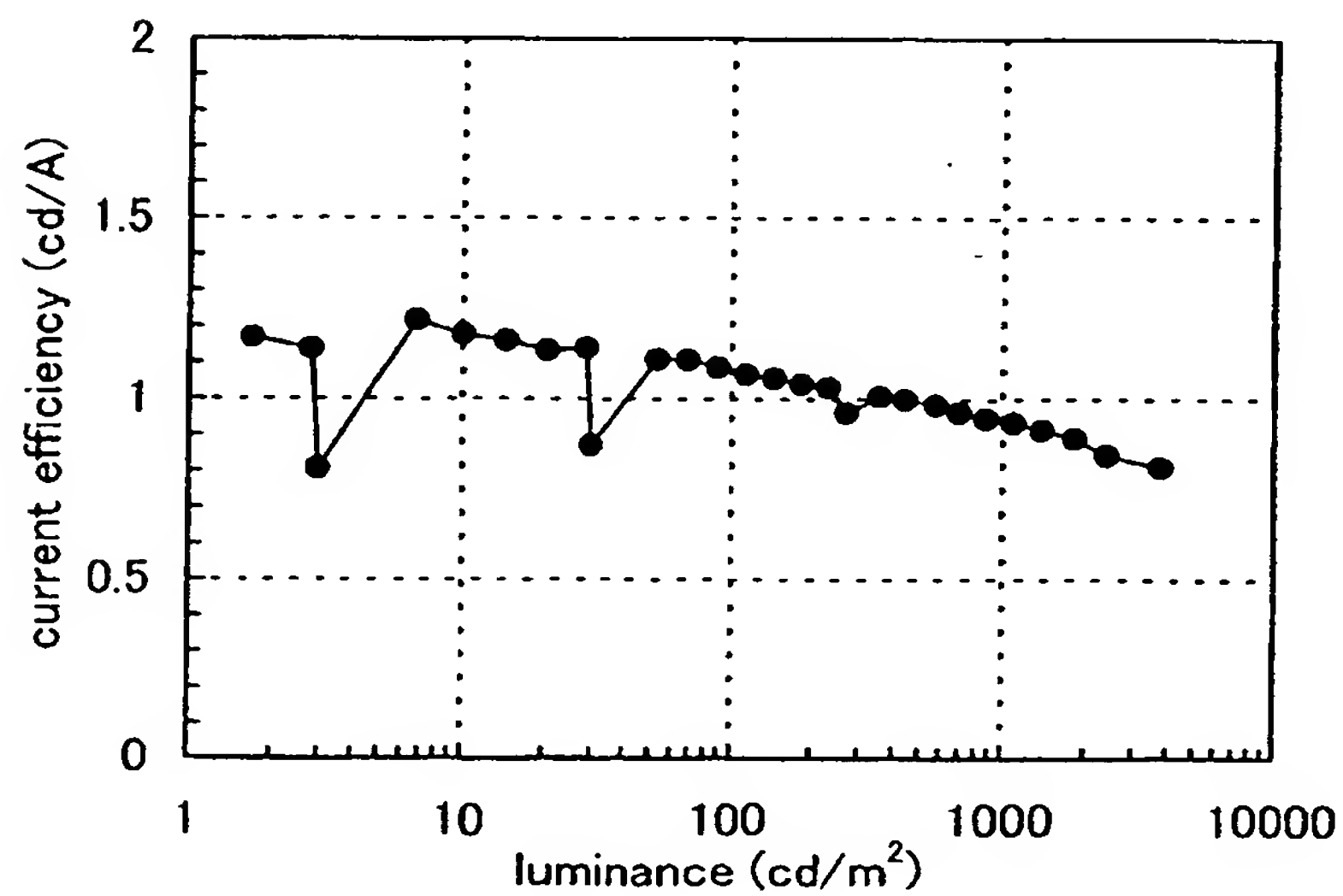


FIG. 20C



21/48

FIG. 21

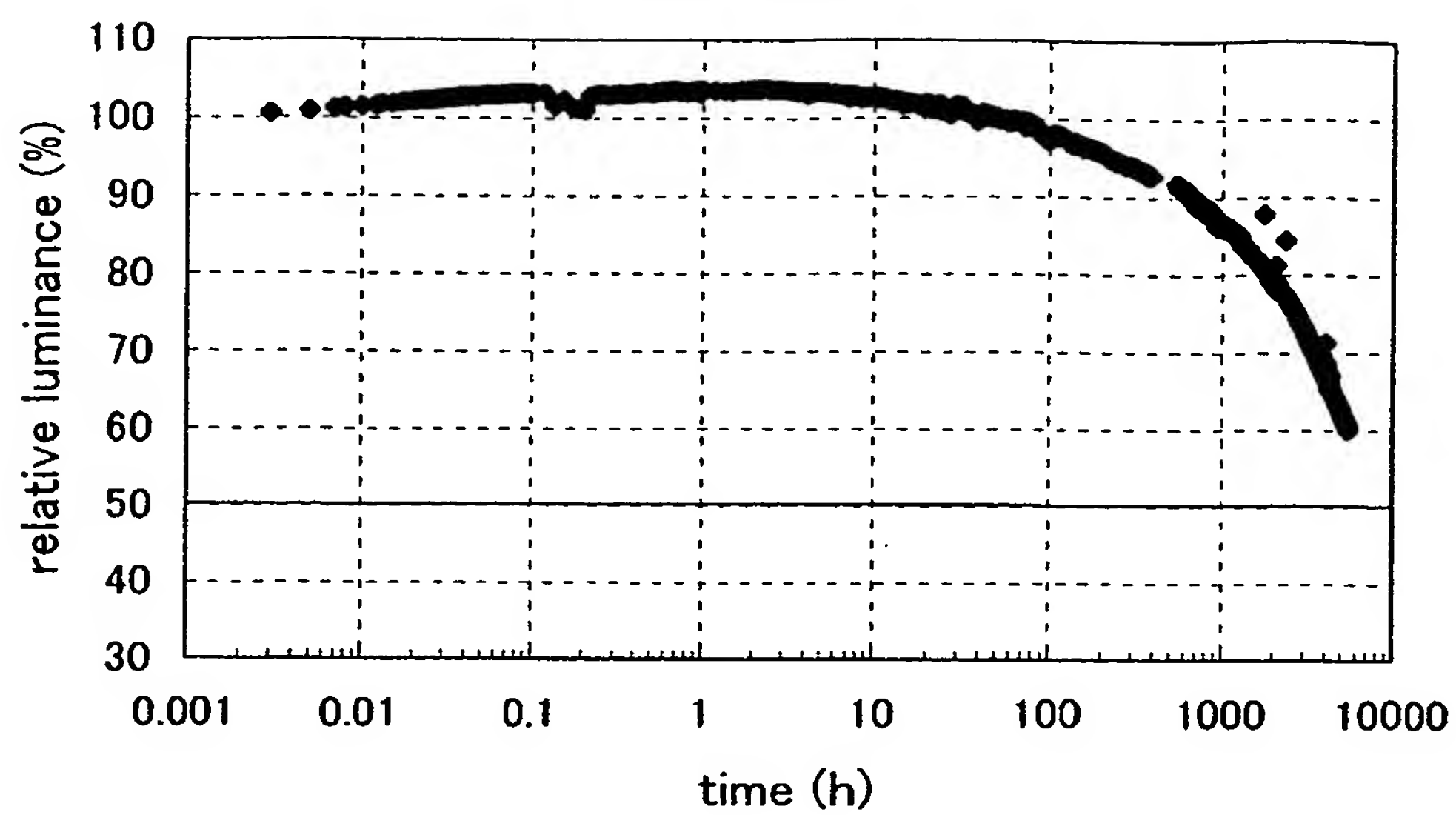


FIG. 22

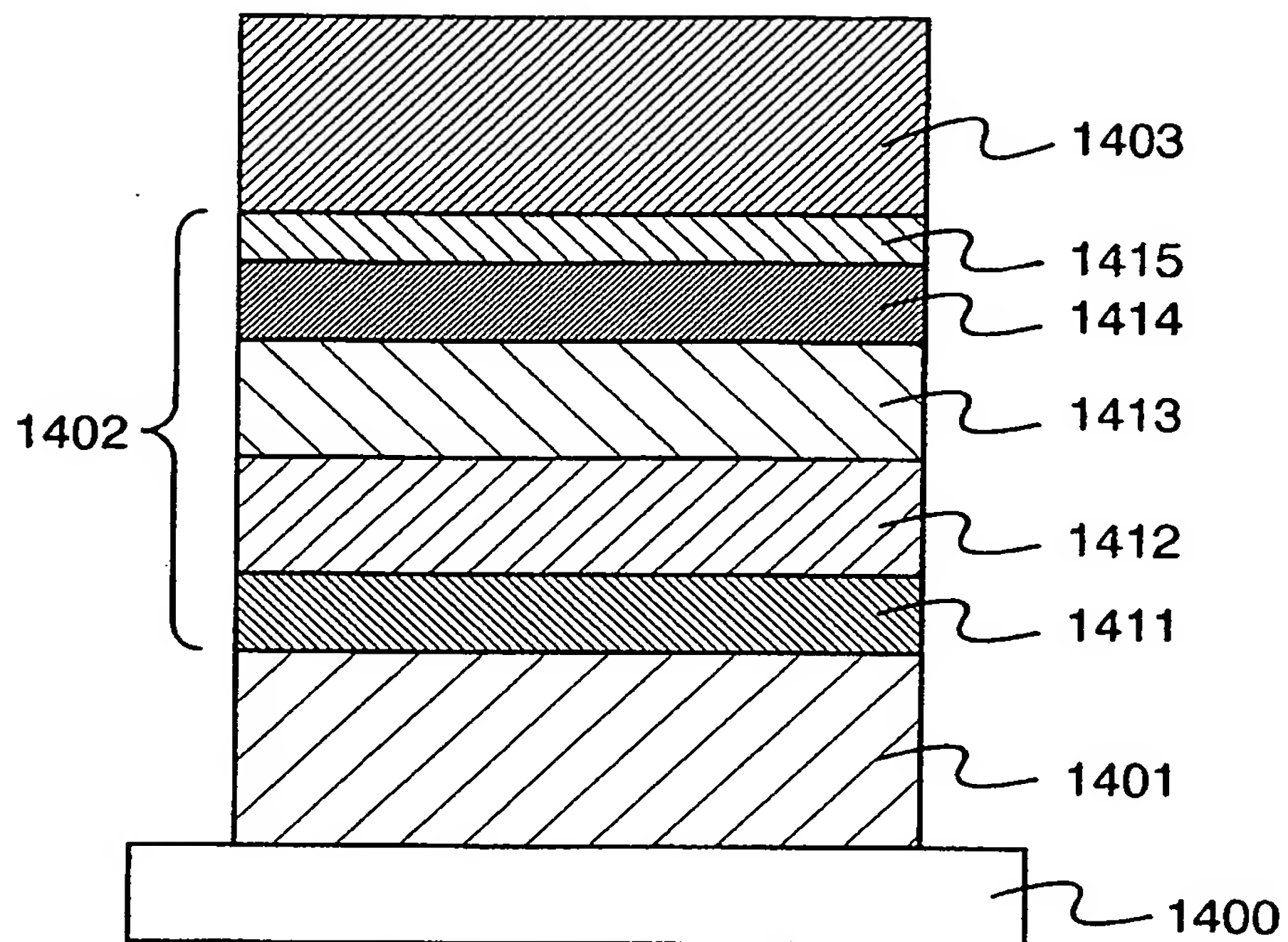


FIG. 23A

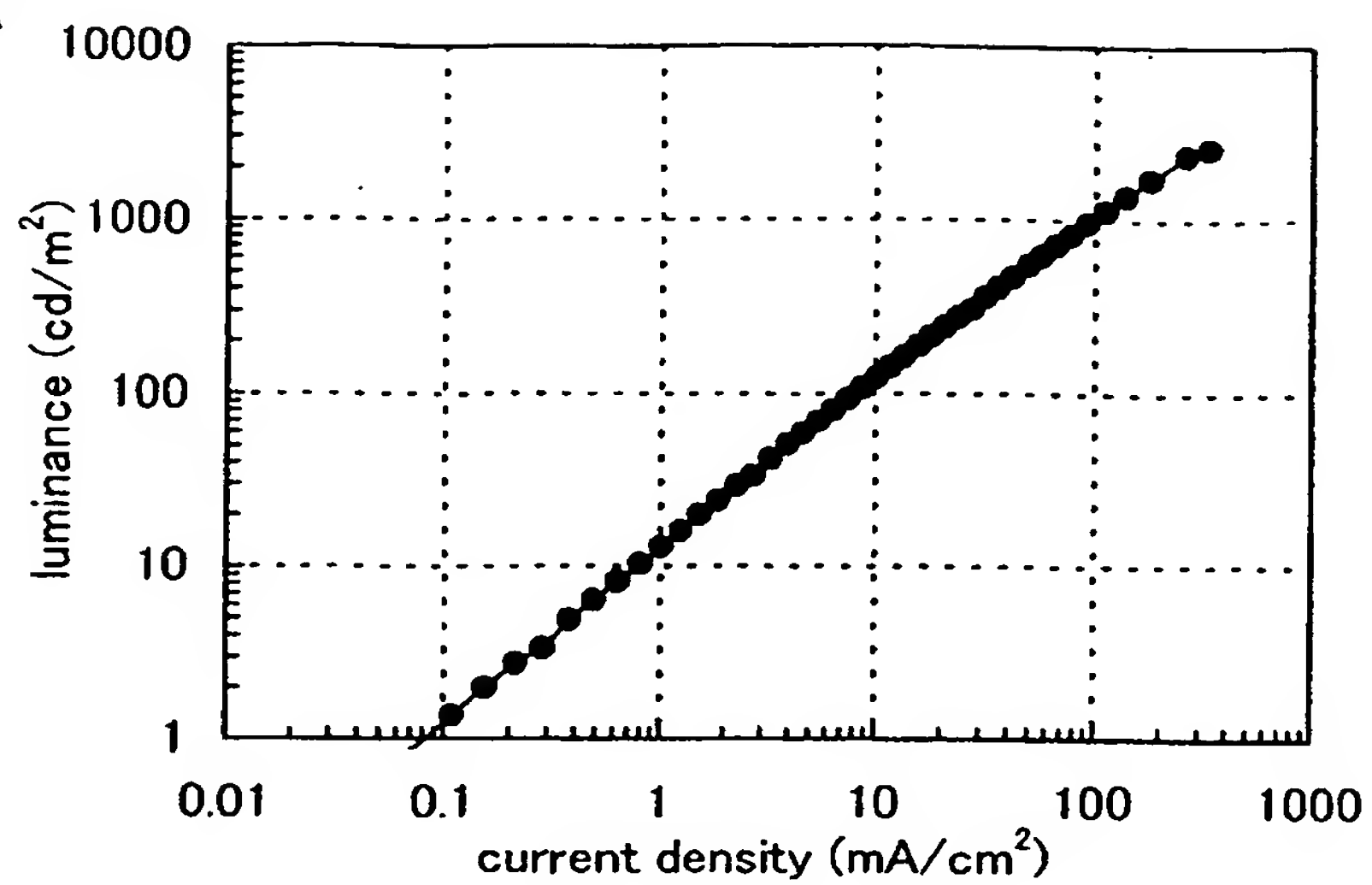


FIG. 23B

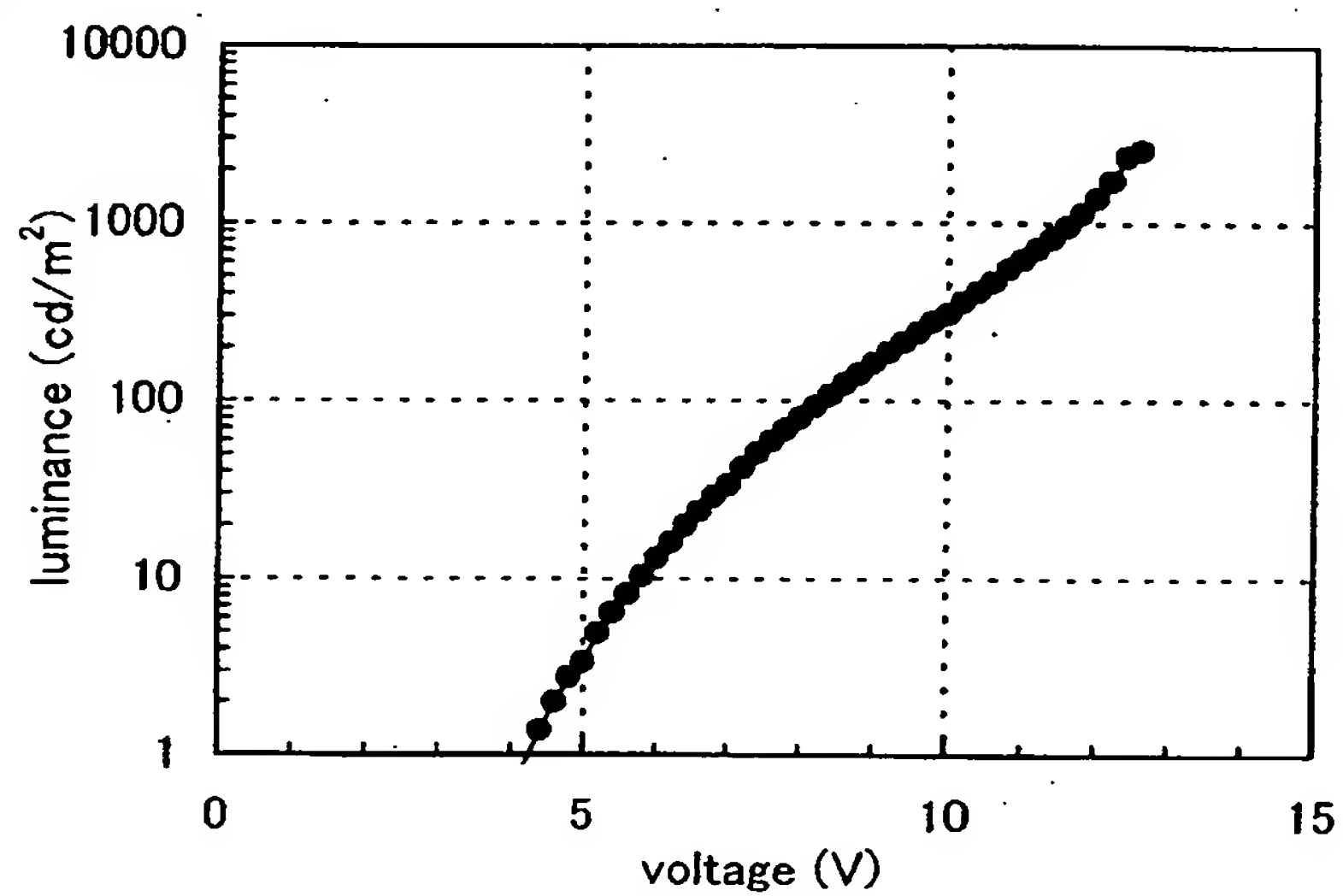
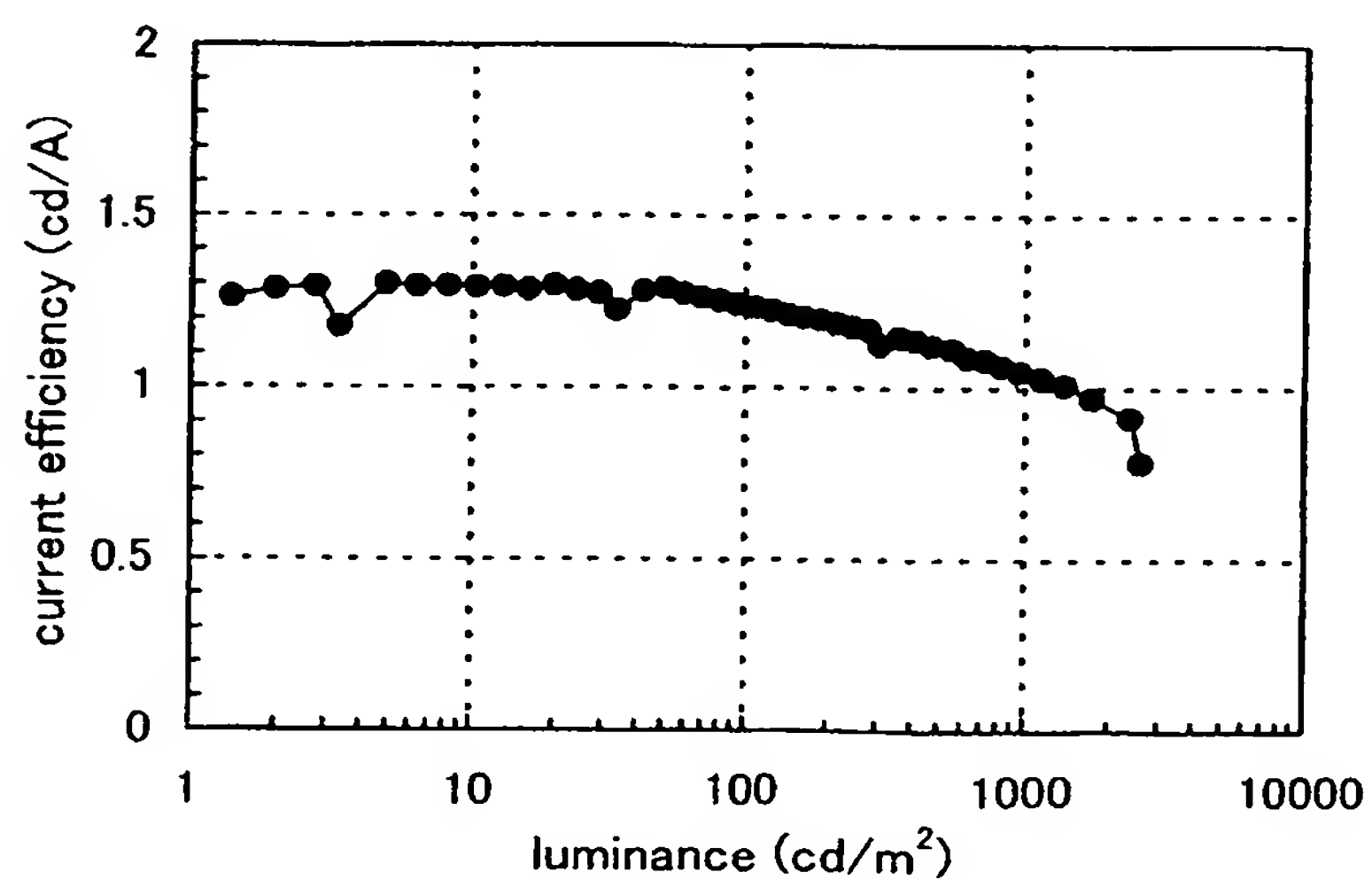
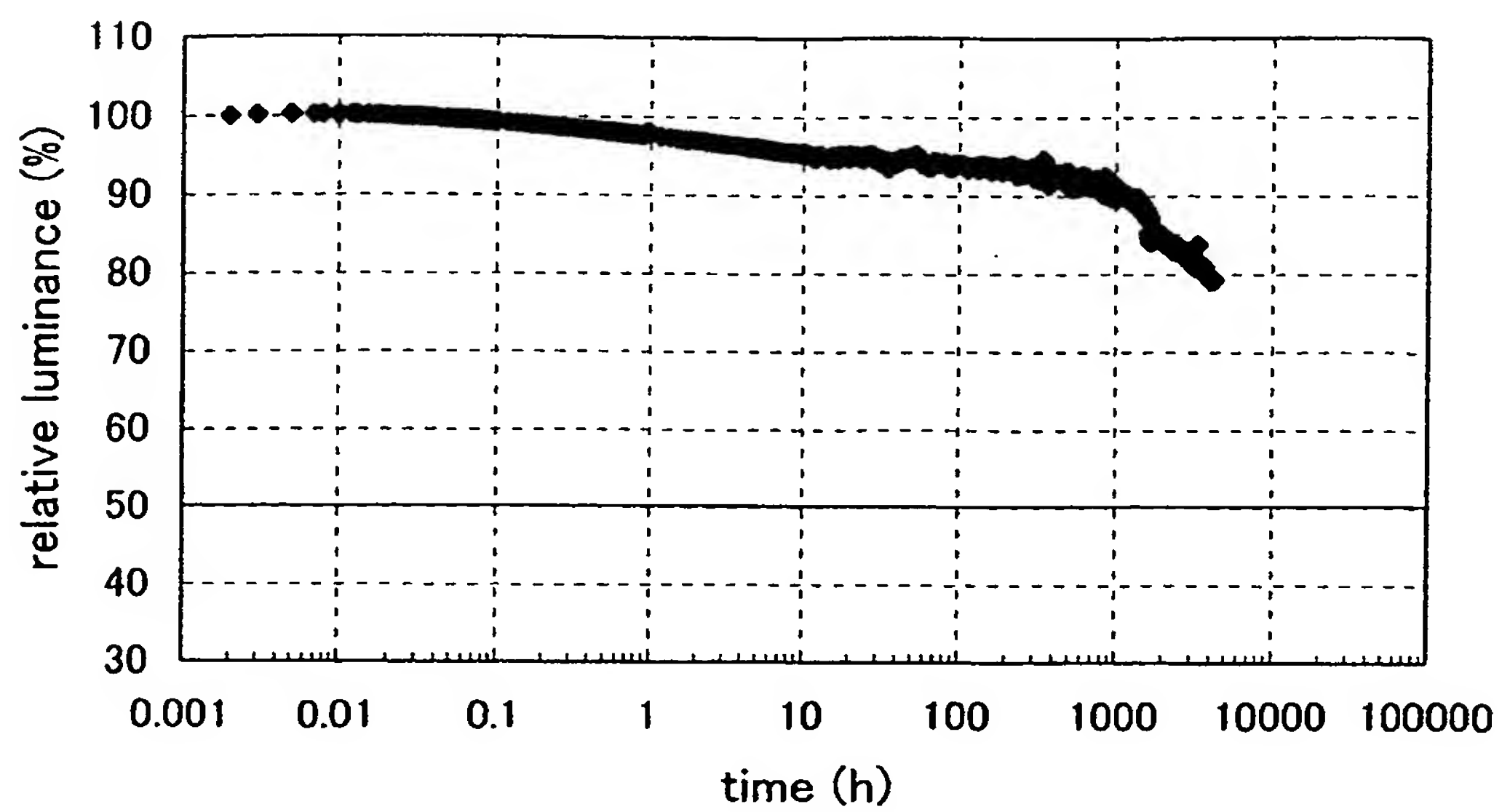


FIG. 23C



24/48

FIG. 24



25/48

FIG. 25A

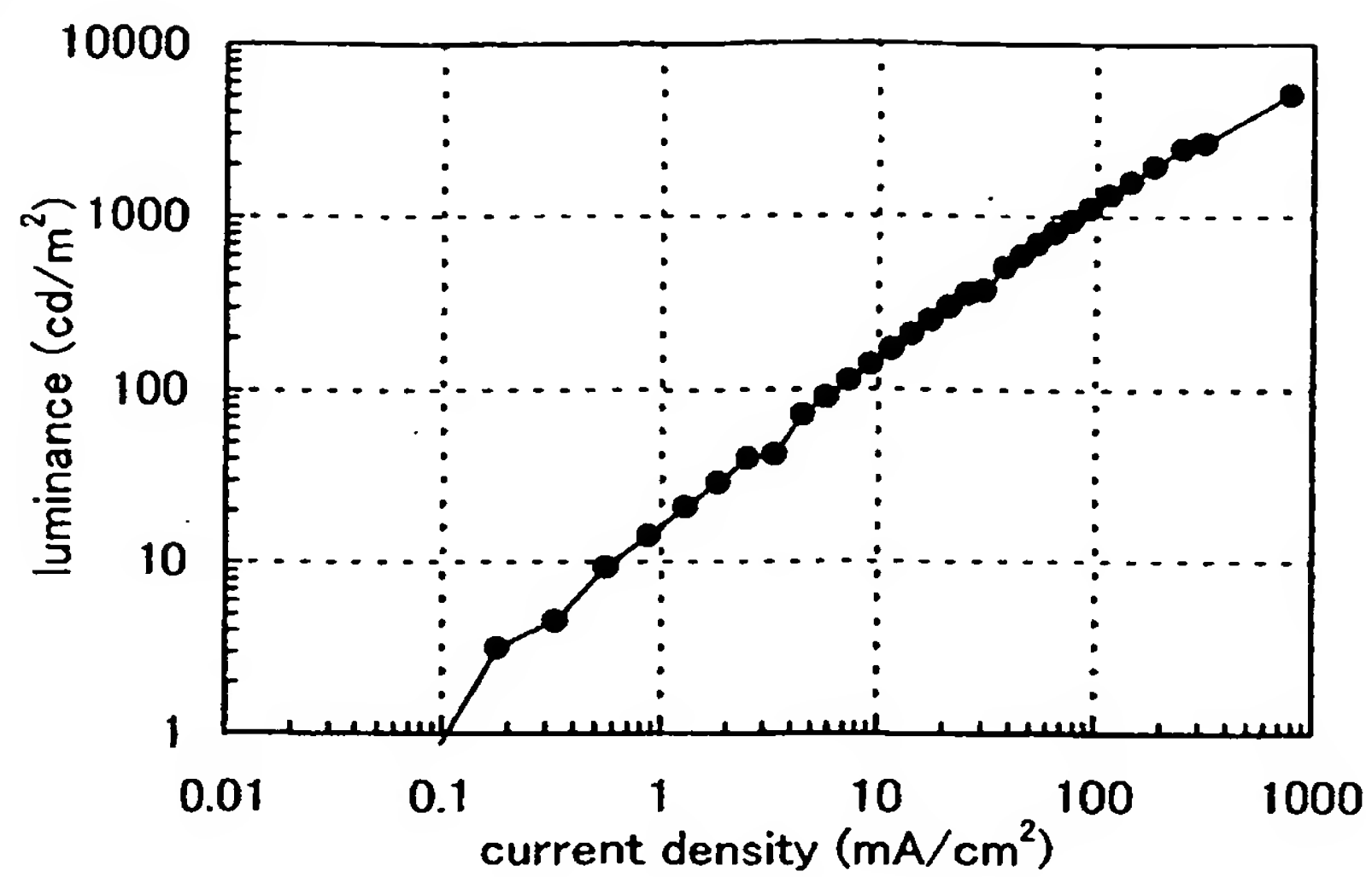


FIG. 25B

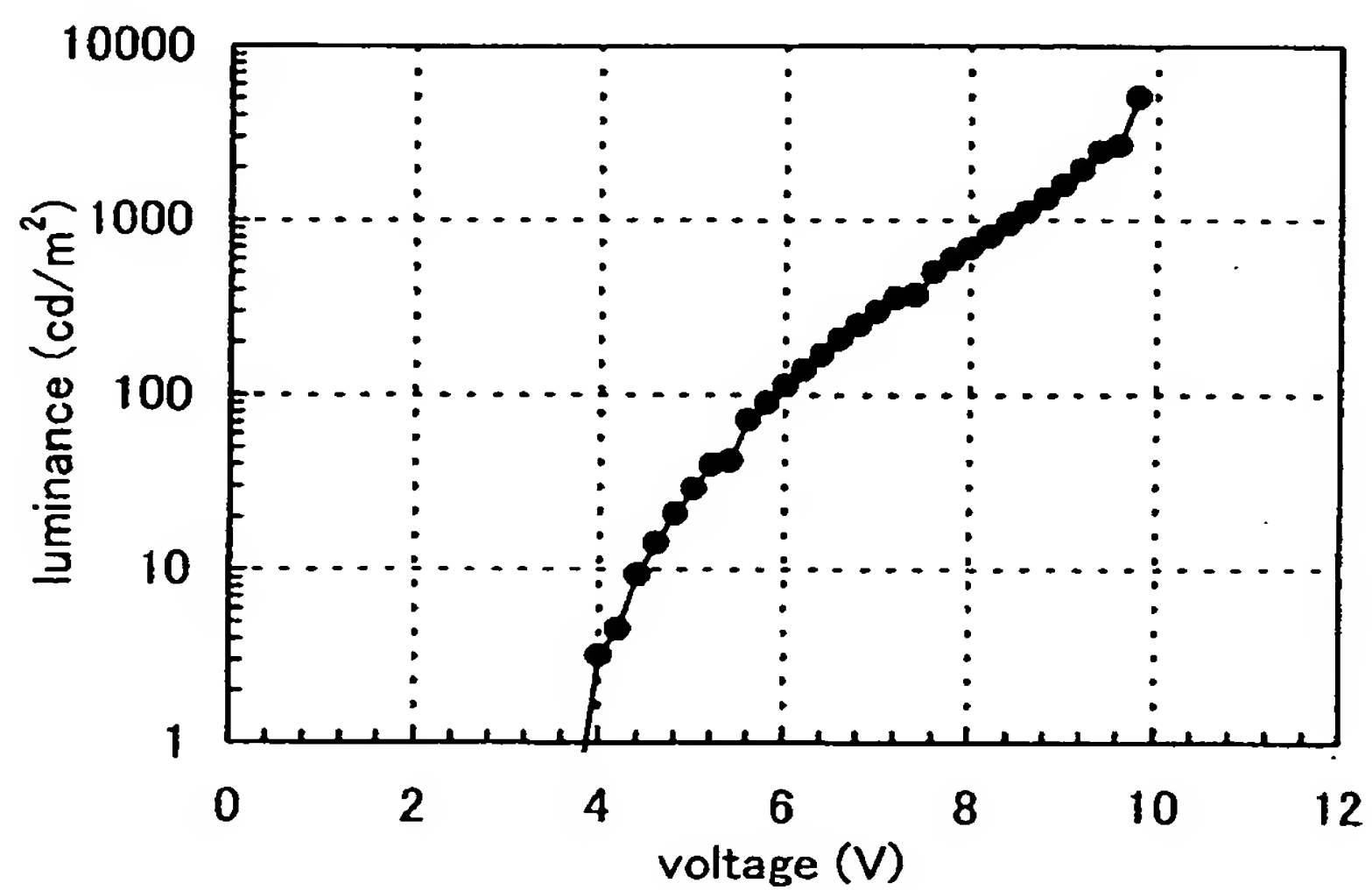
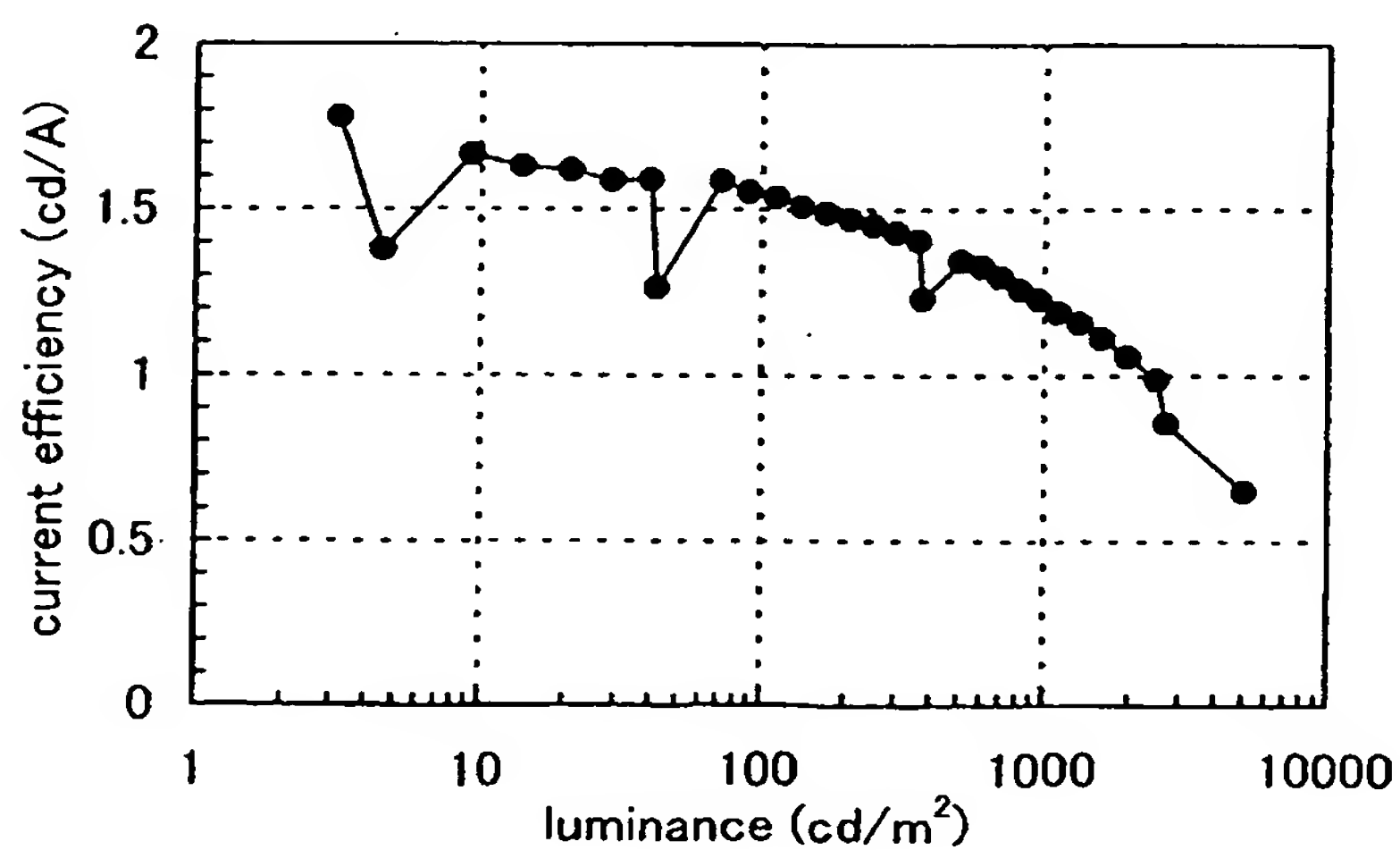
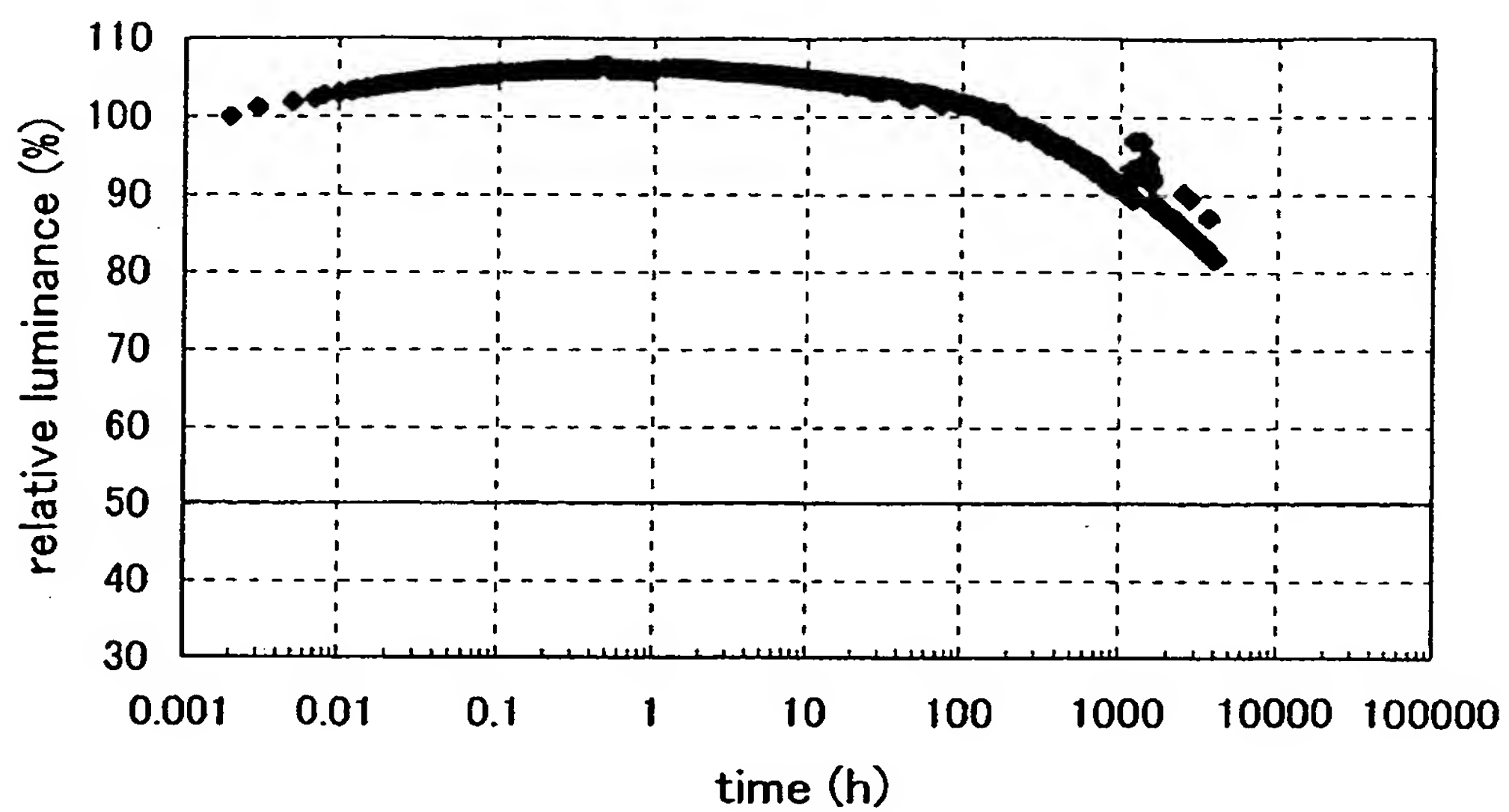


FIG. 25C



26/48

FIG. 26



27/48

FIG. 27A

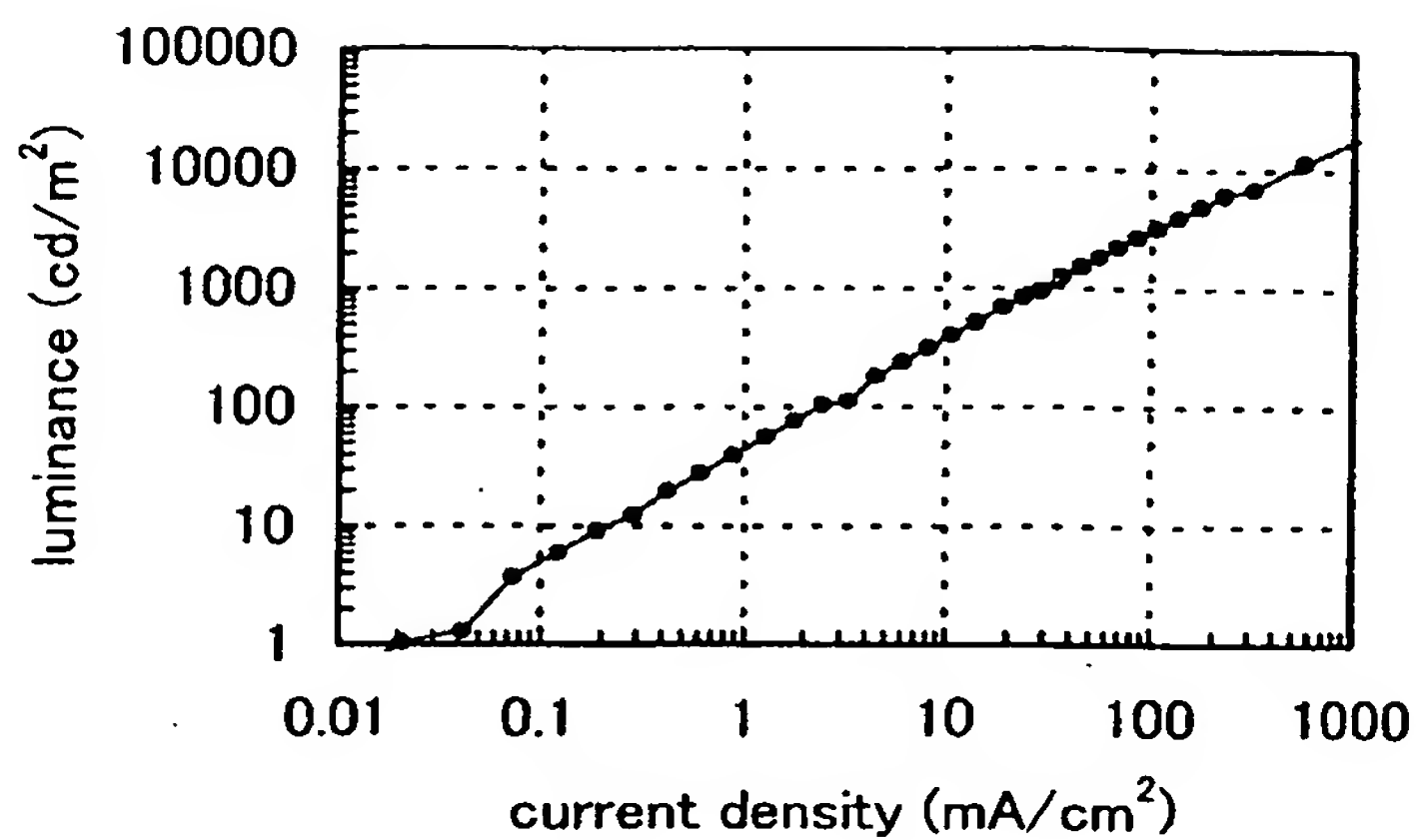


FIG. 27B

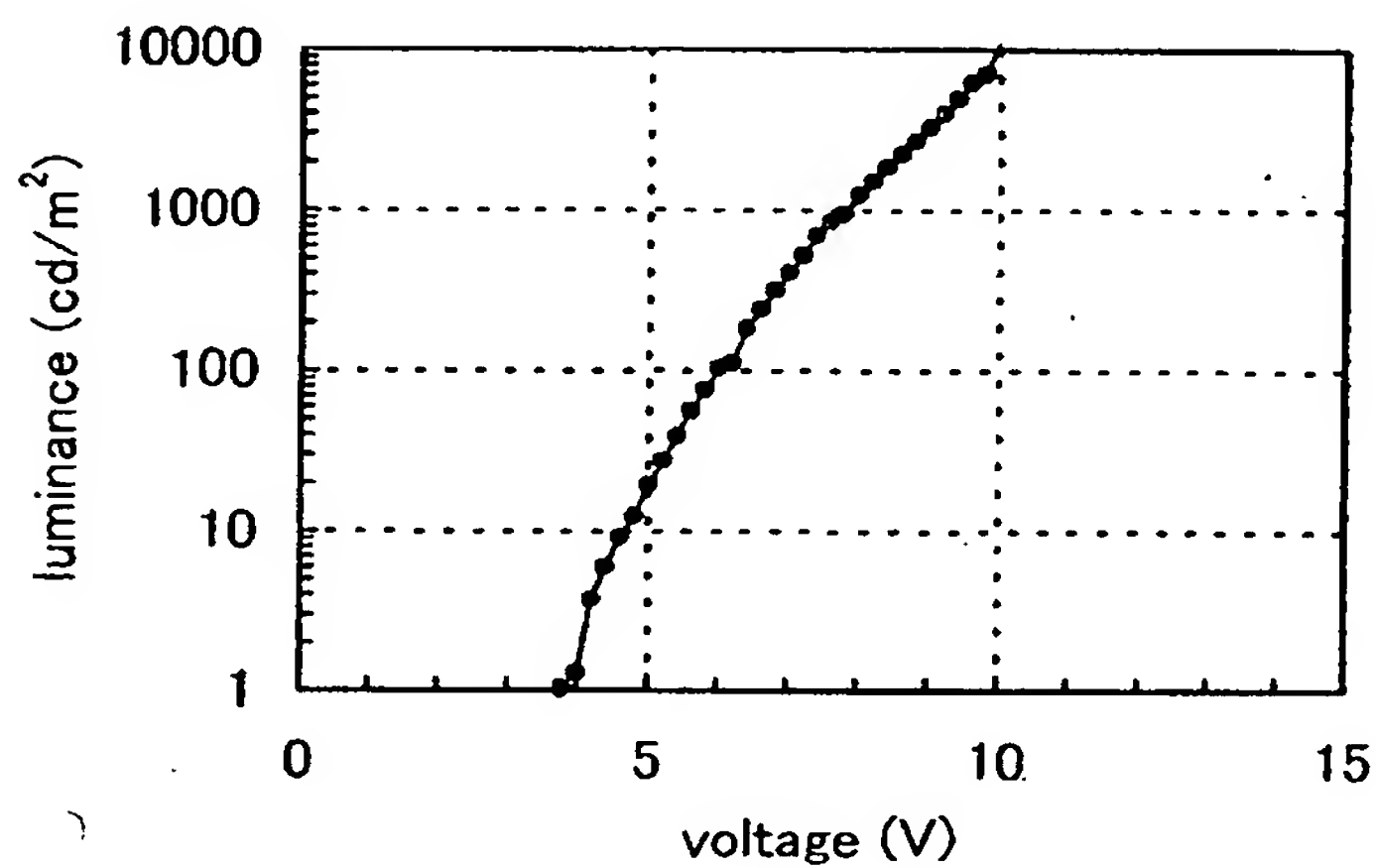
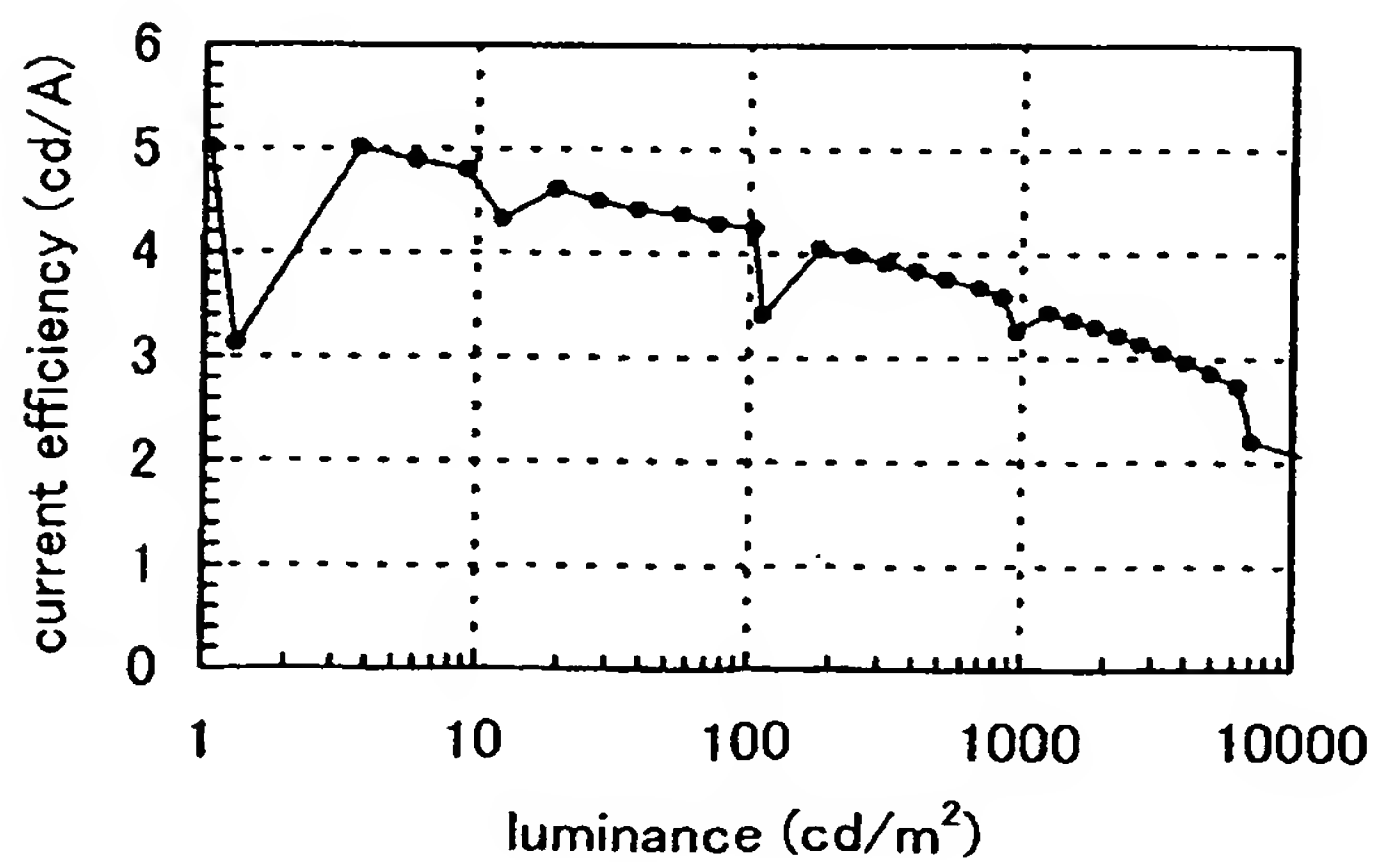
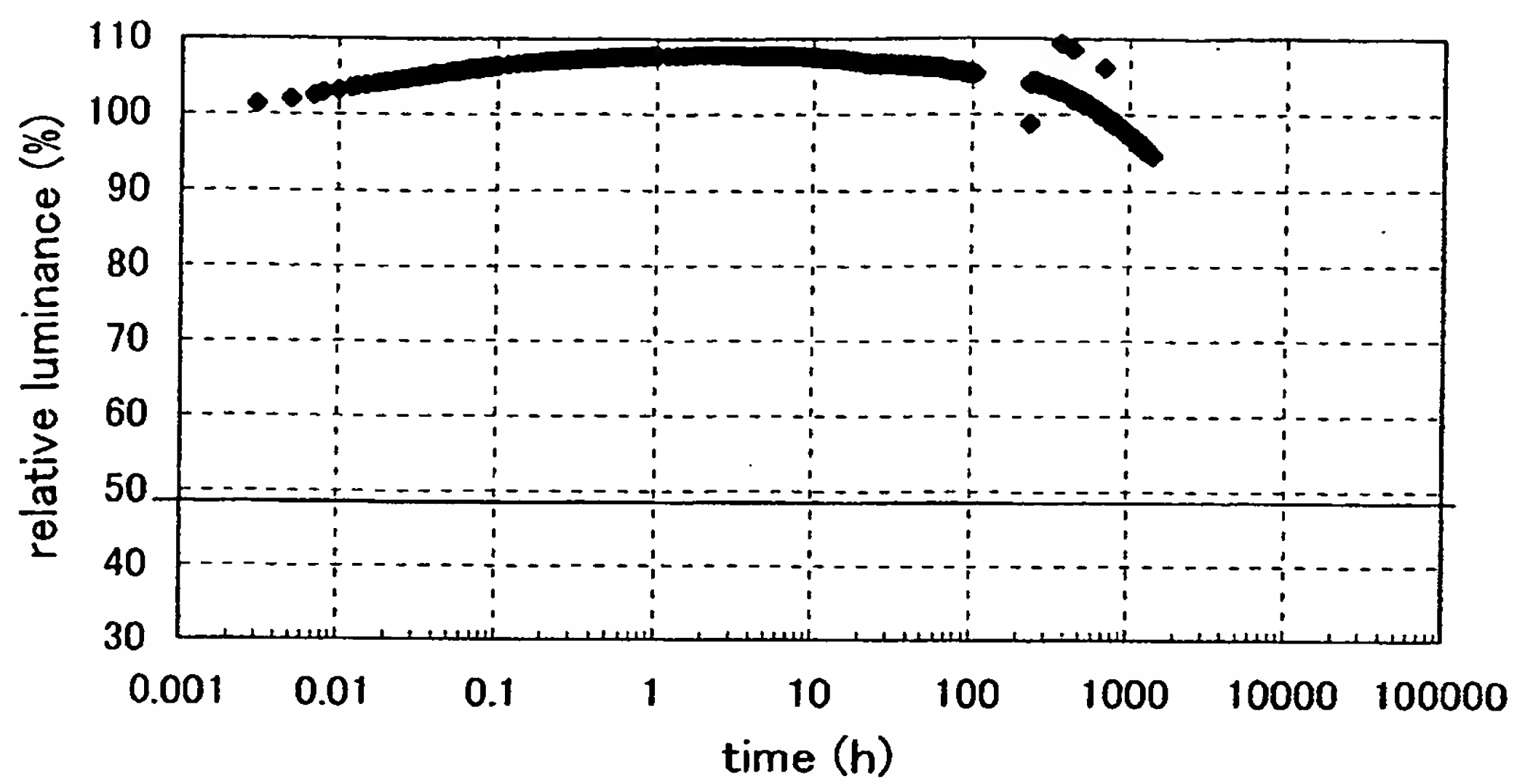


FIG. 27C



28/48

FIG. 28



29/48

FIG. 29A

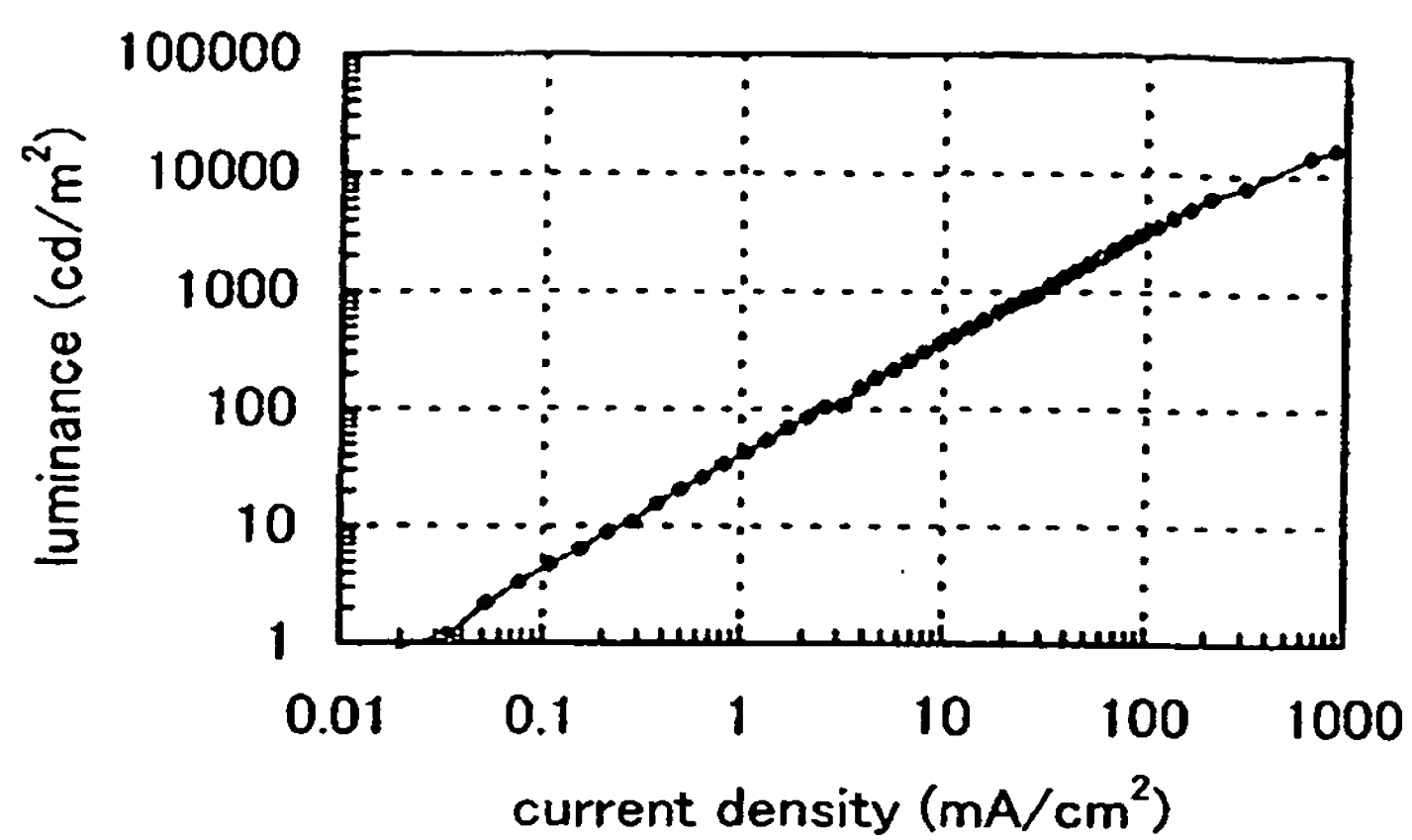


FIG. 29B

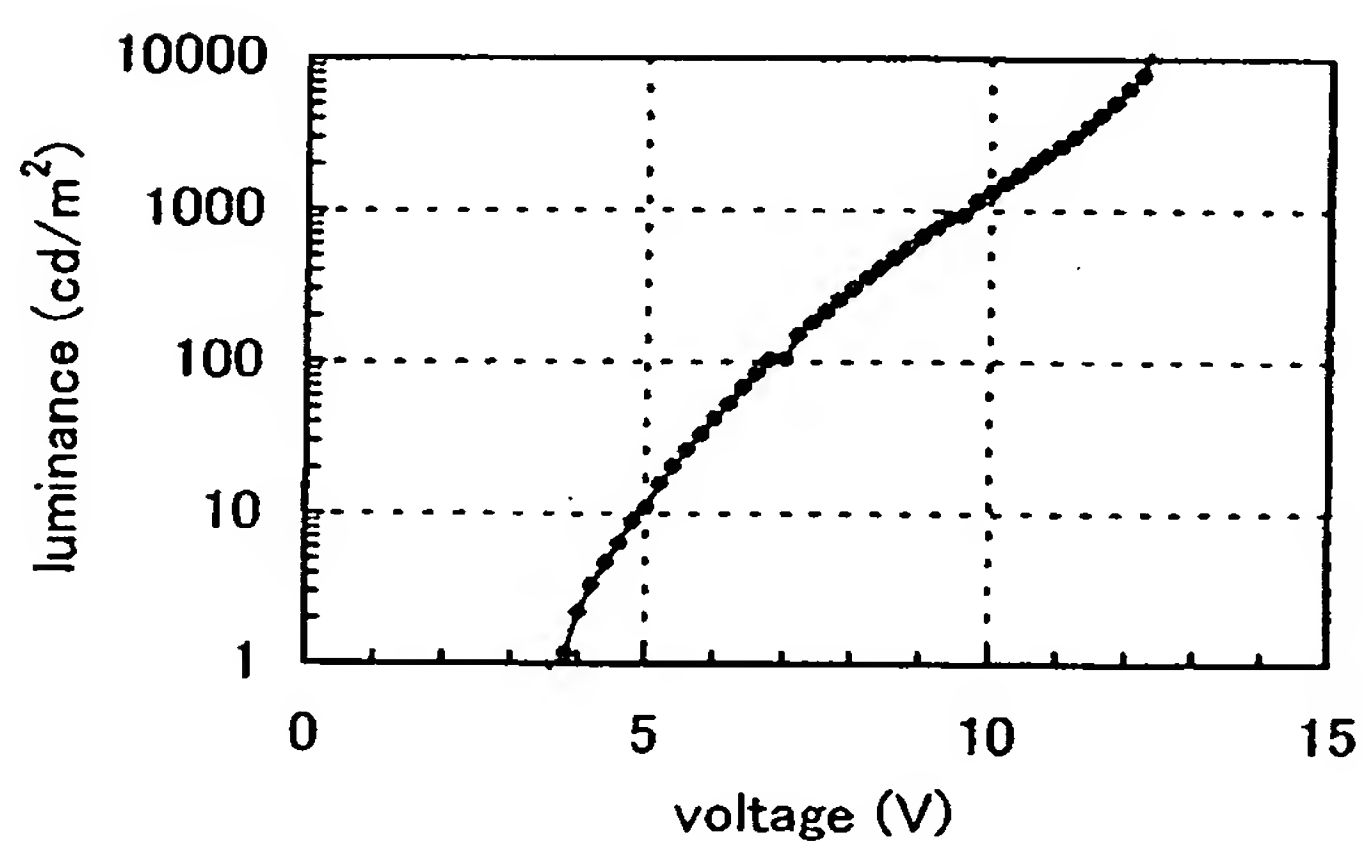
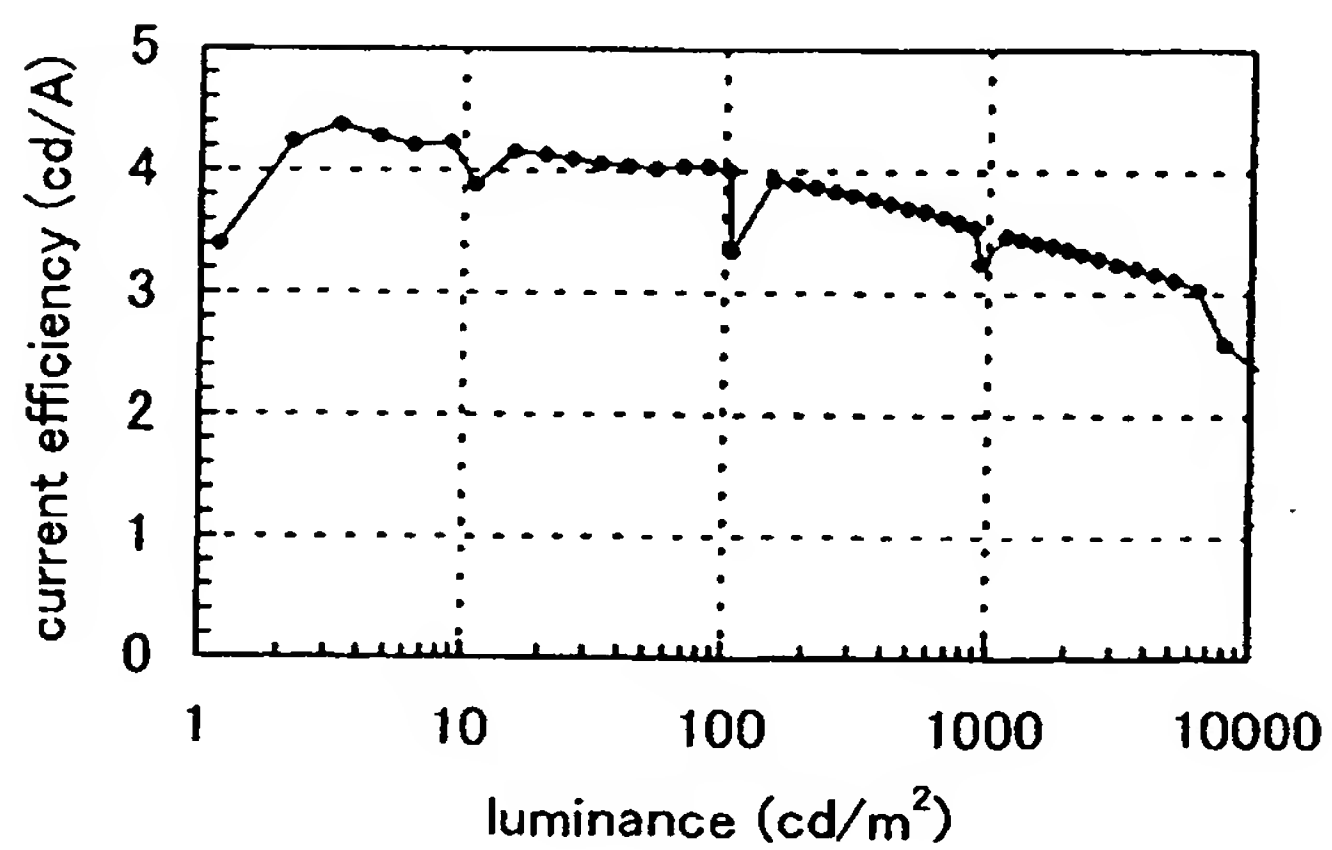
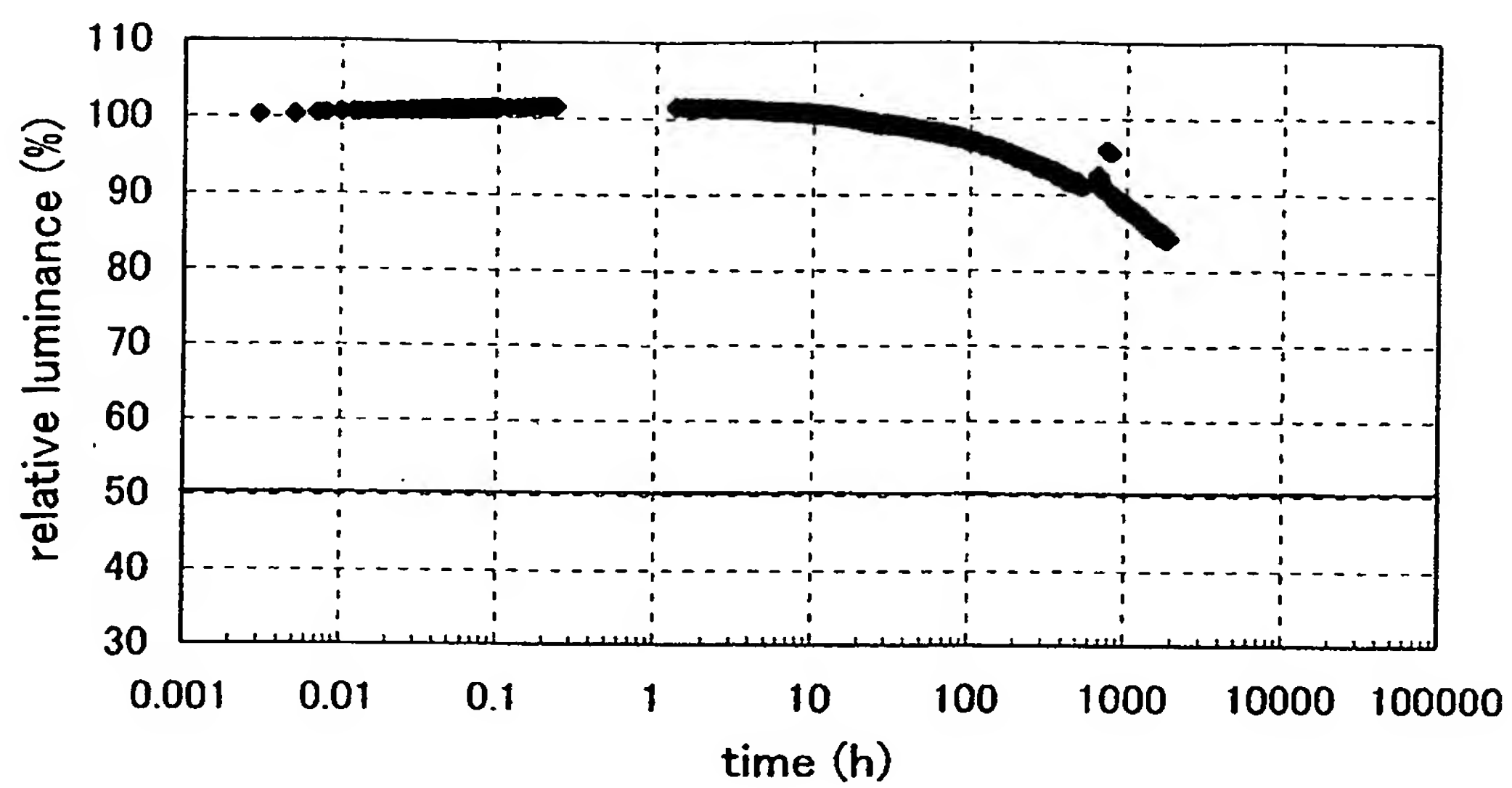


FIG. 29C



30/48

FIG. 30



31/48

FIG. 31A

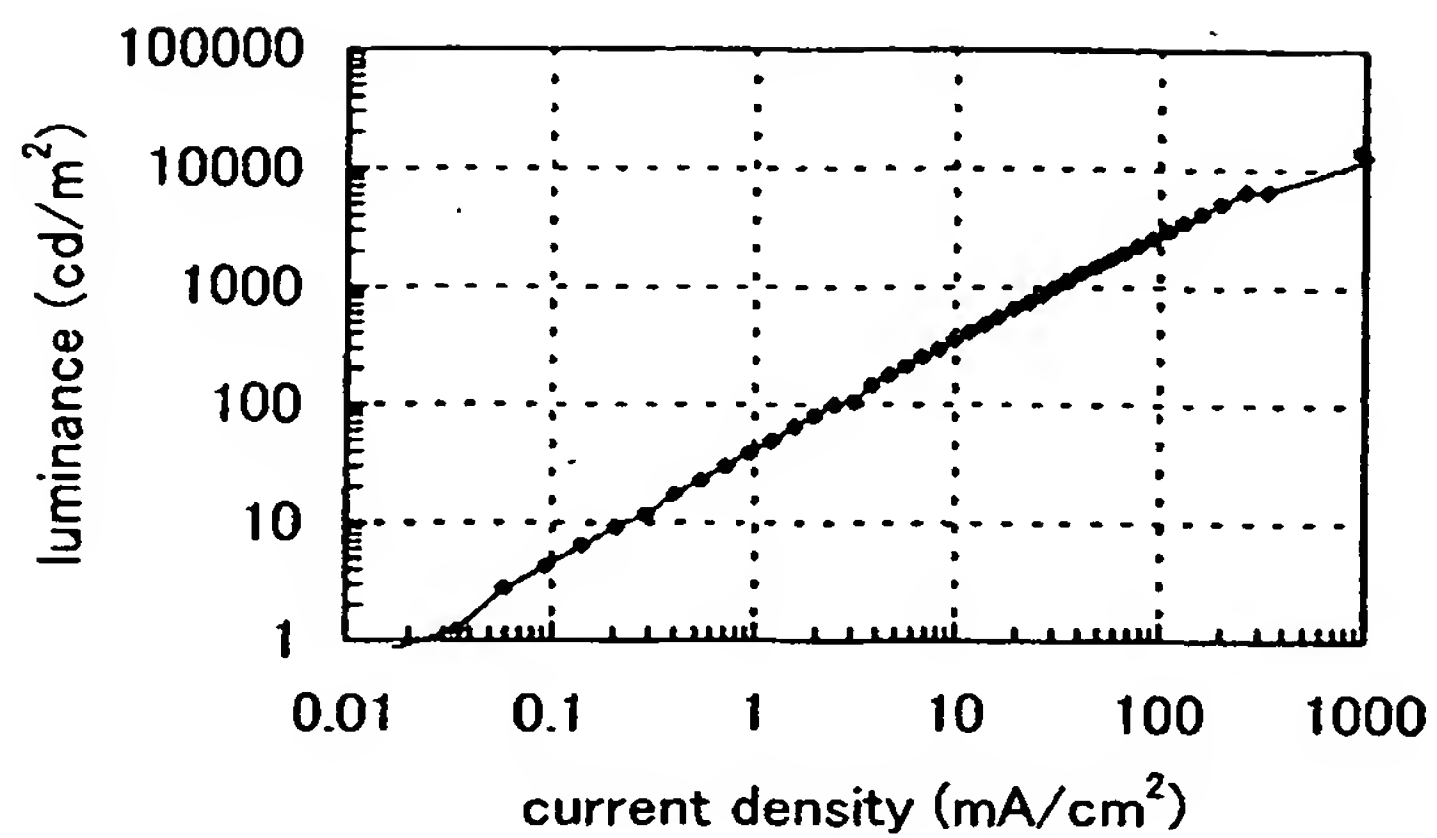


FIG. 31B

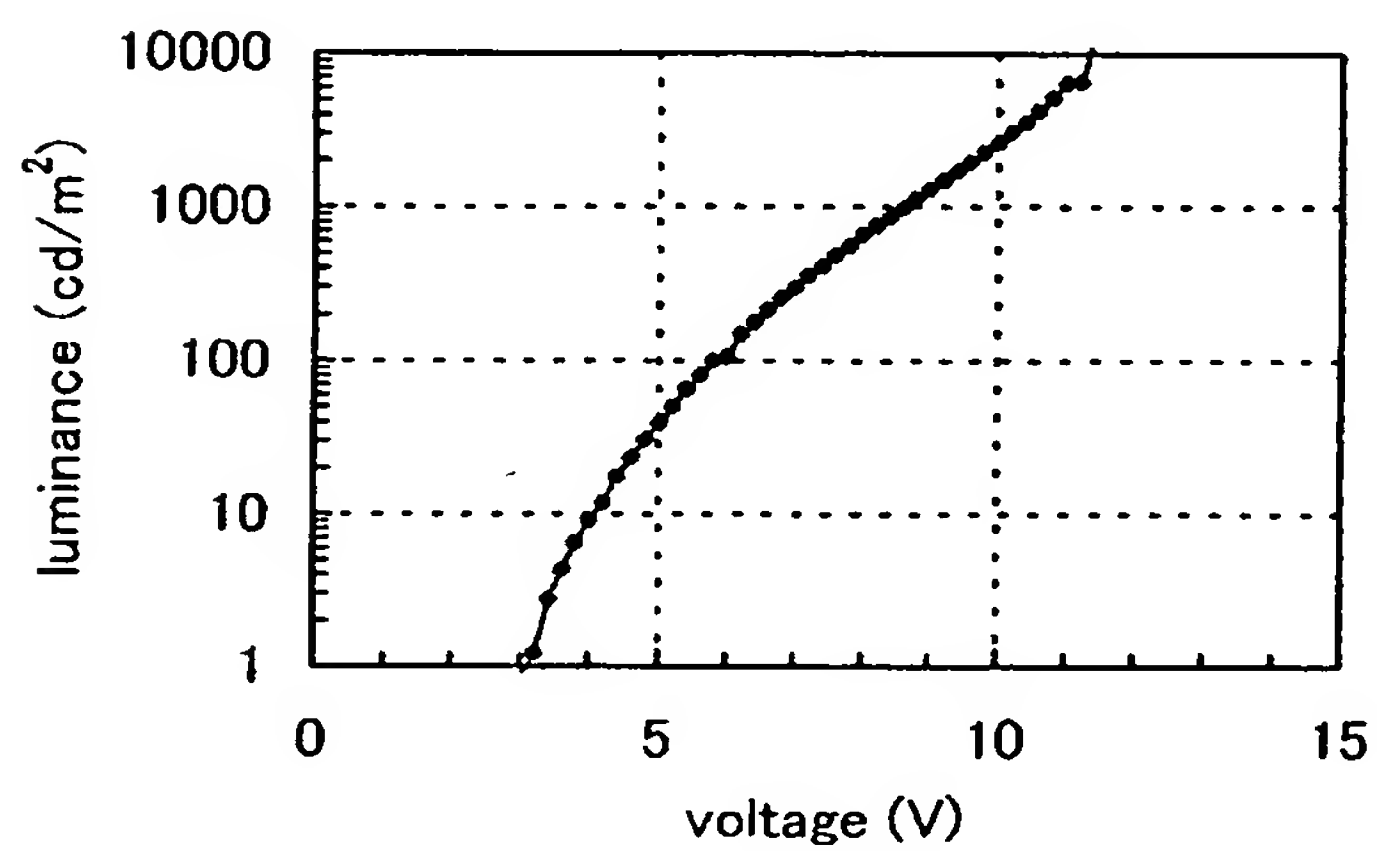
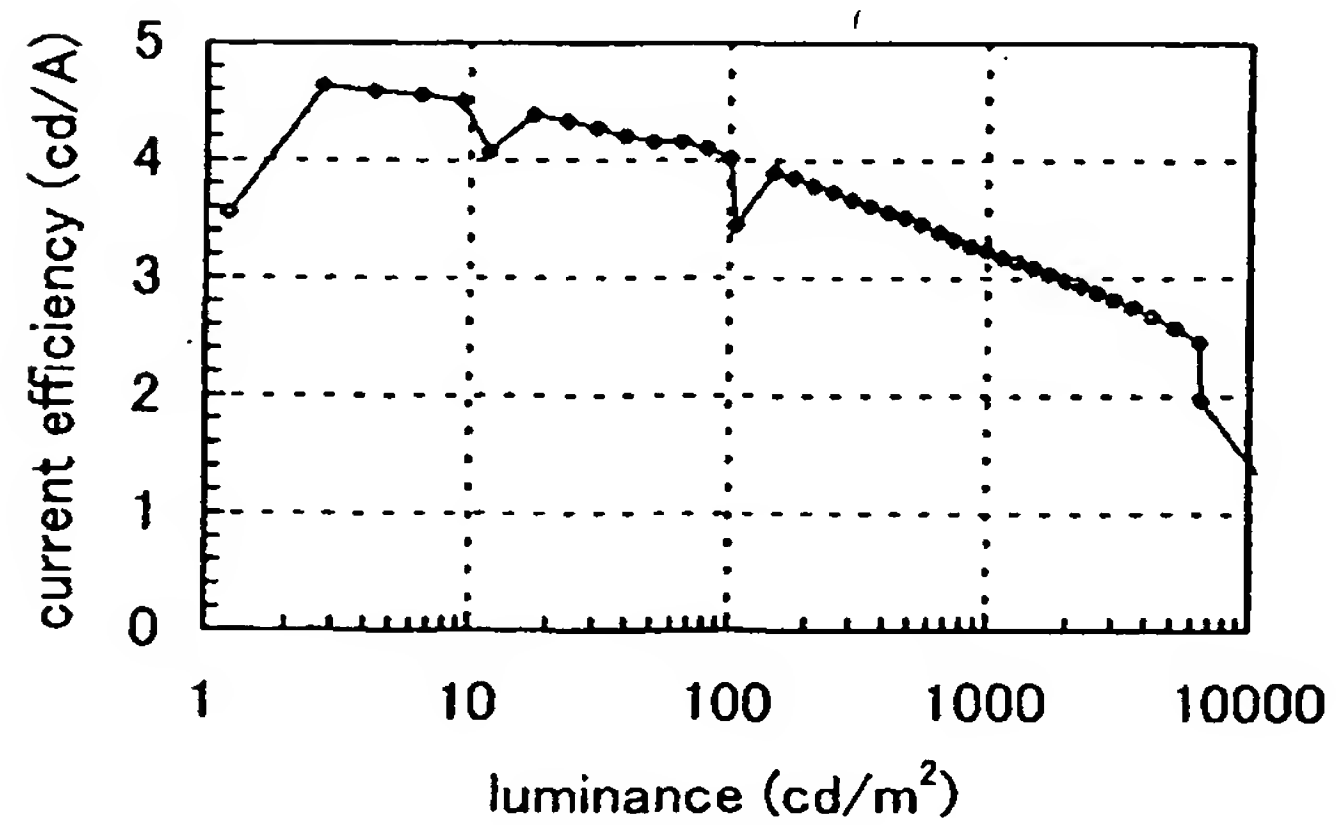
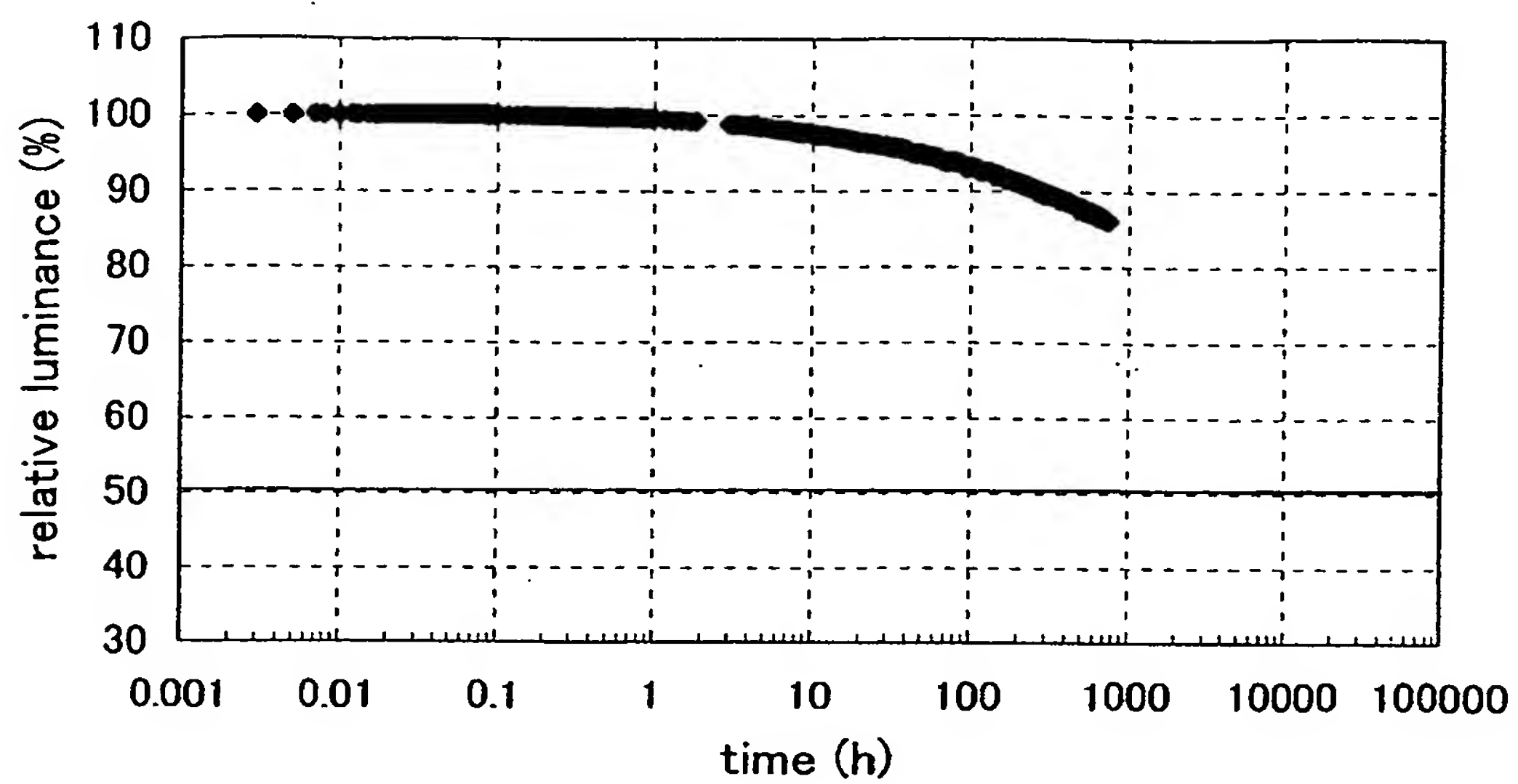


FIG. 31C



32/48

FIG. 32



33/48

FIG. 33A

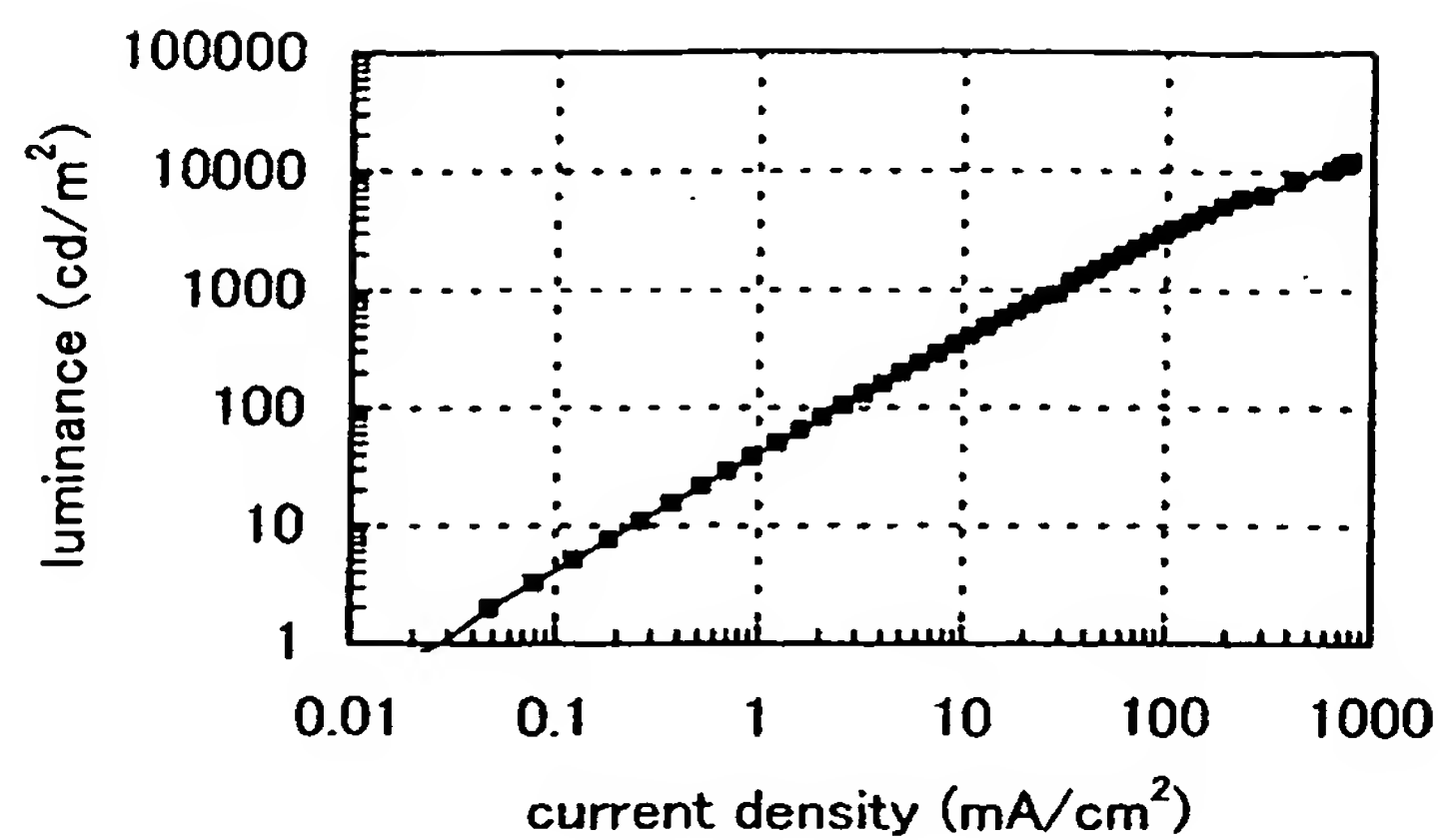


FIG. 33B

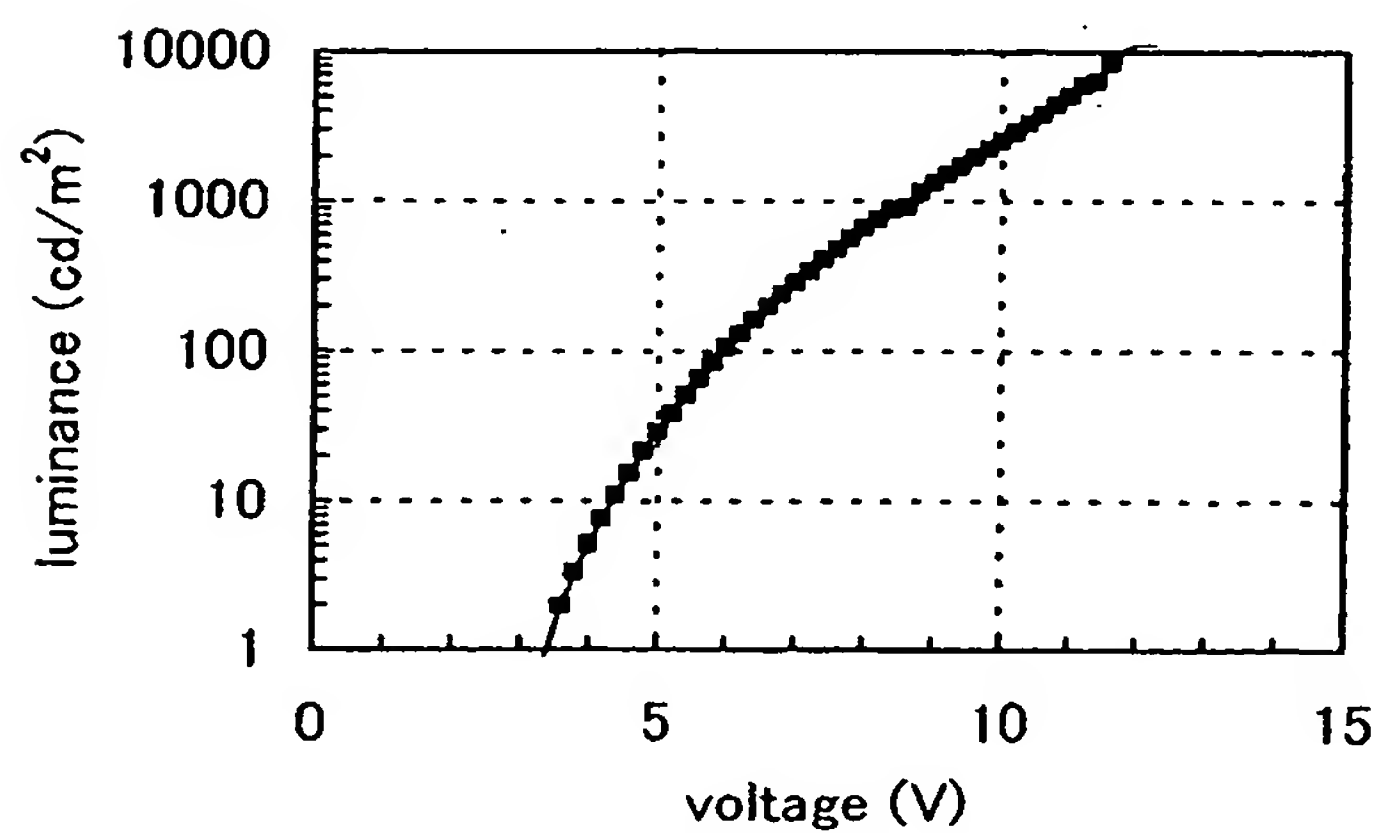
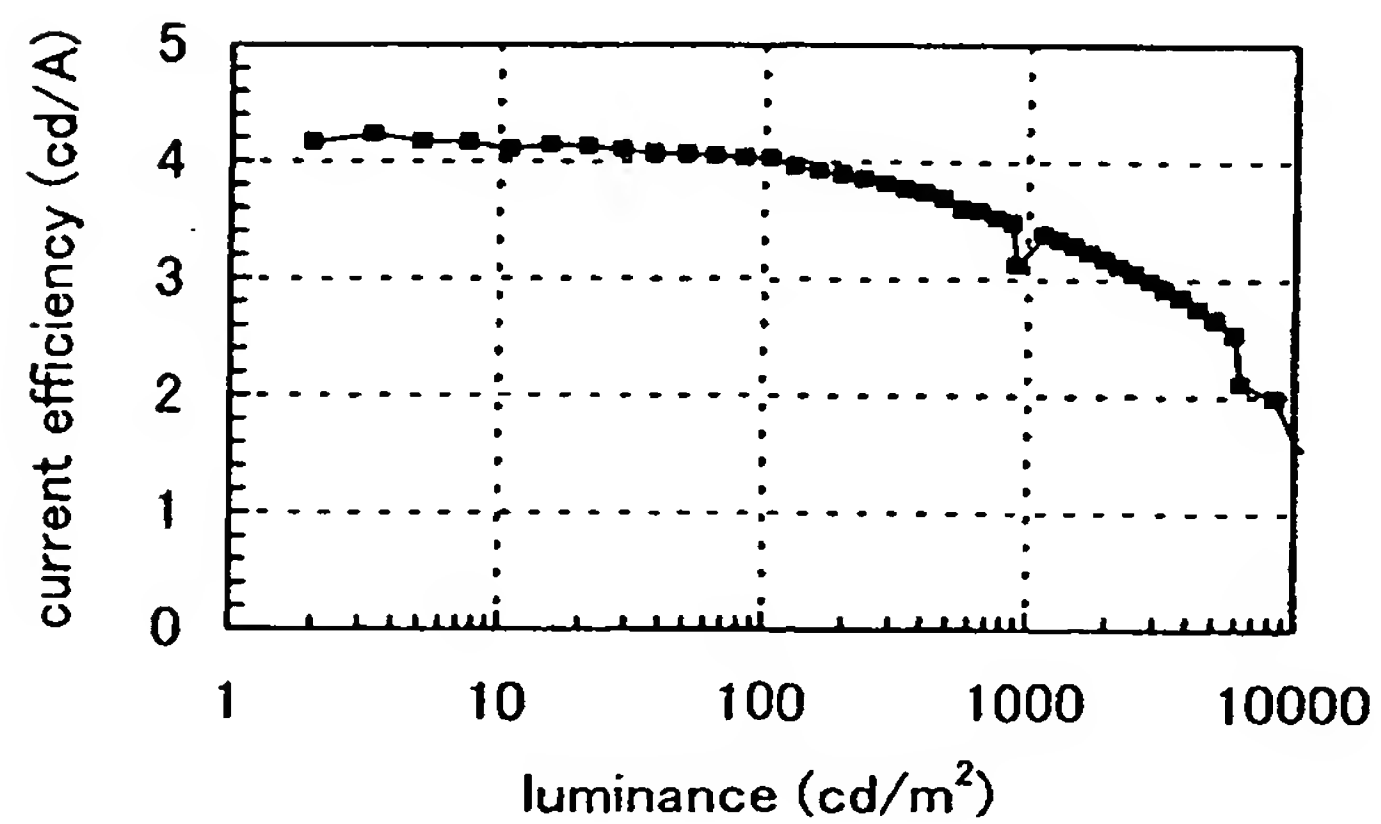
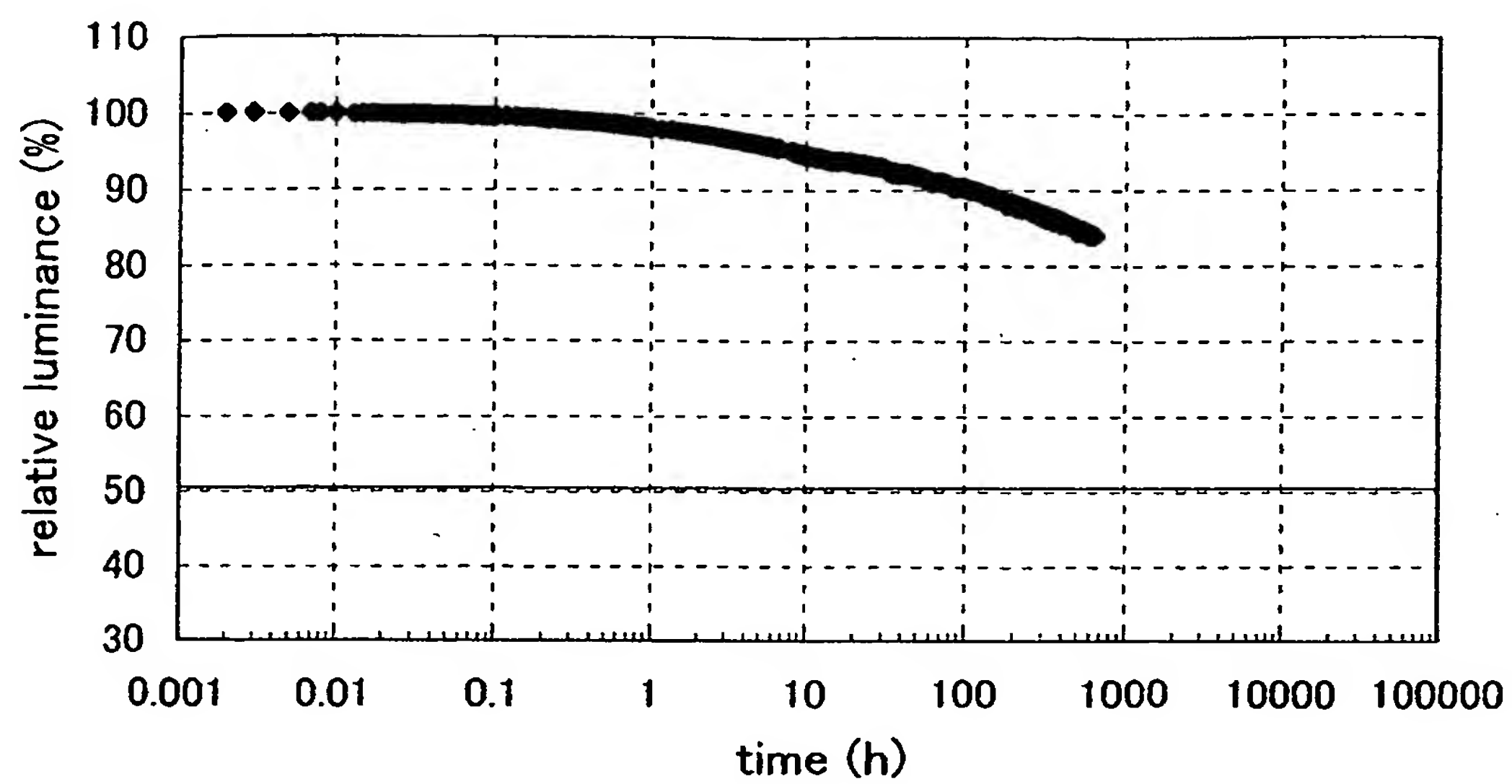


FIG. 33C



34/48

FIG. 34



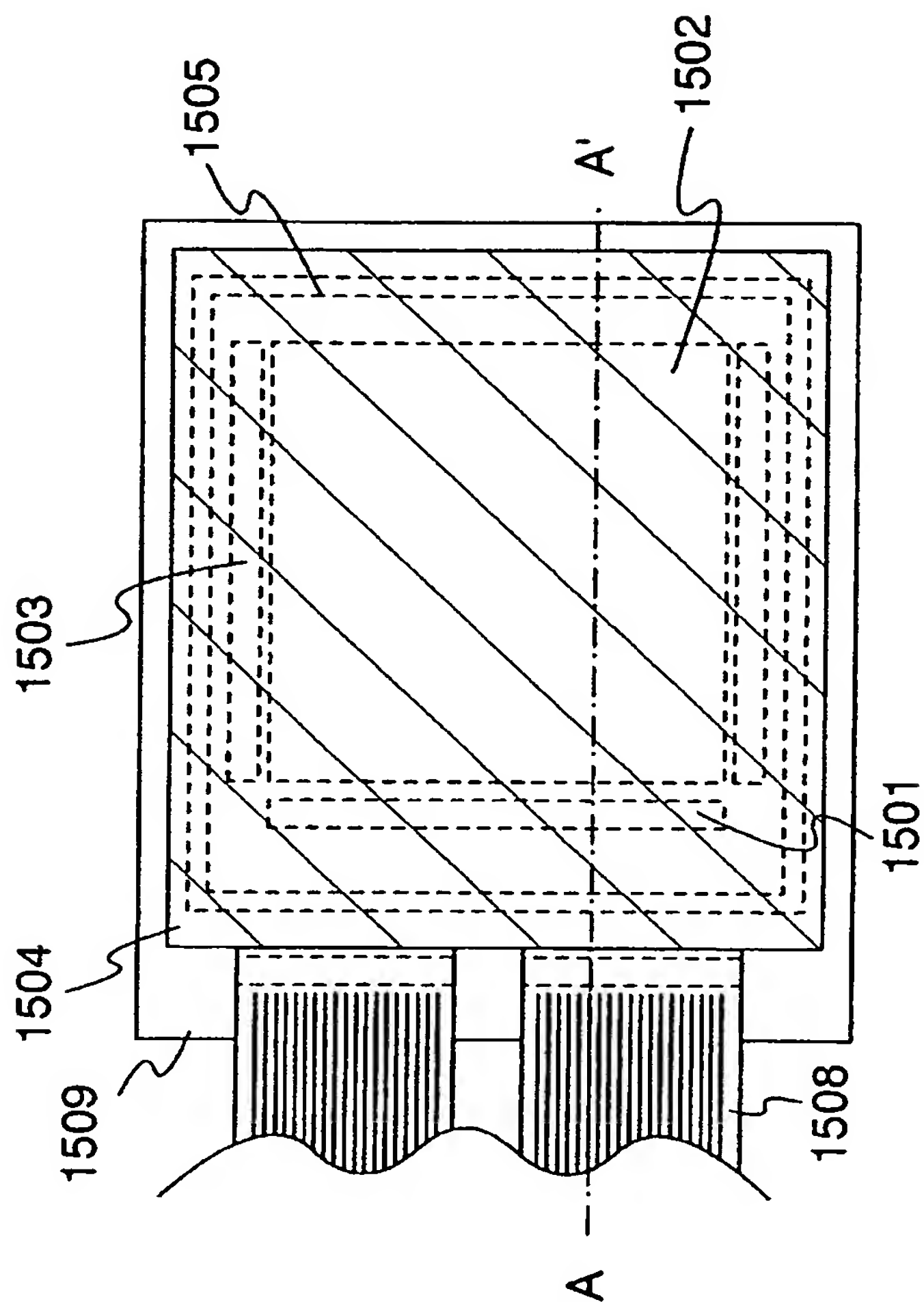


FIG. 35A

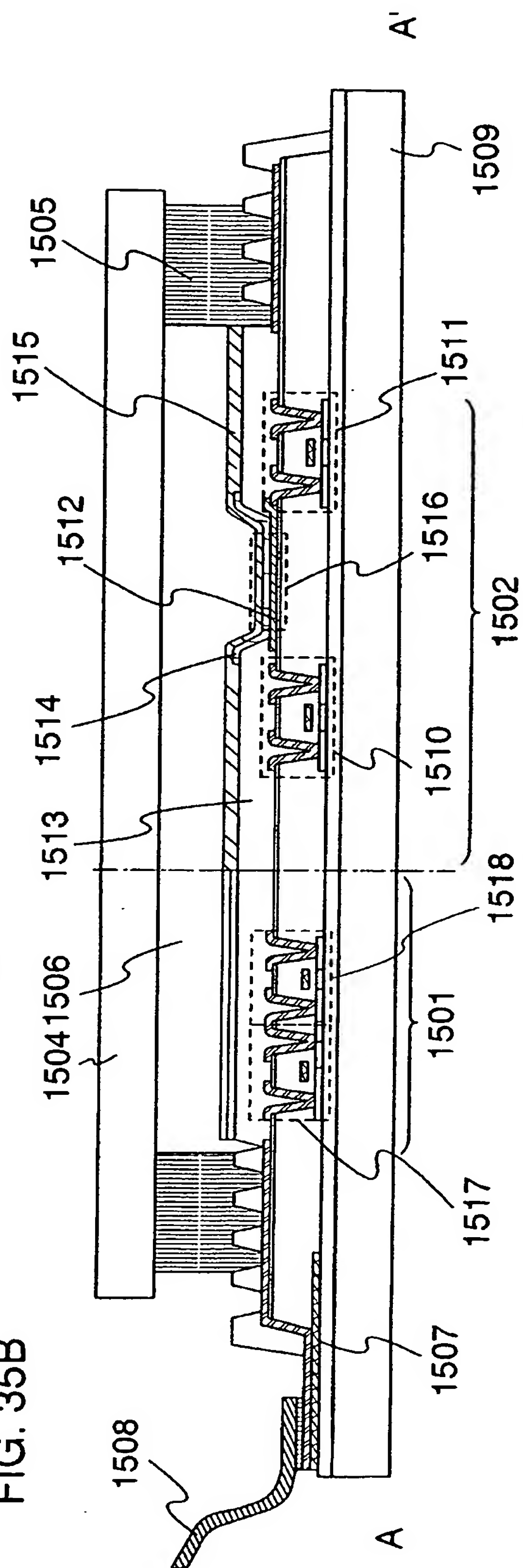


FIG. 35B

36/48

FIG. 36A

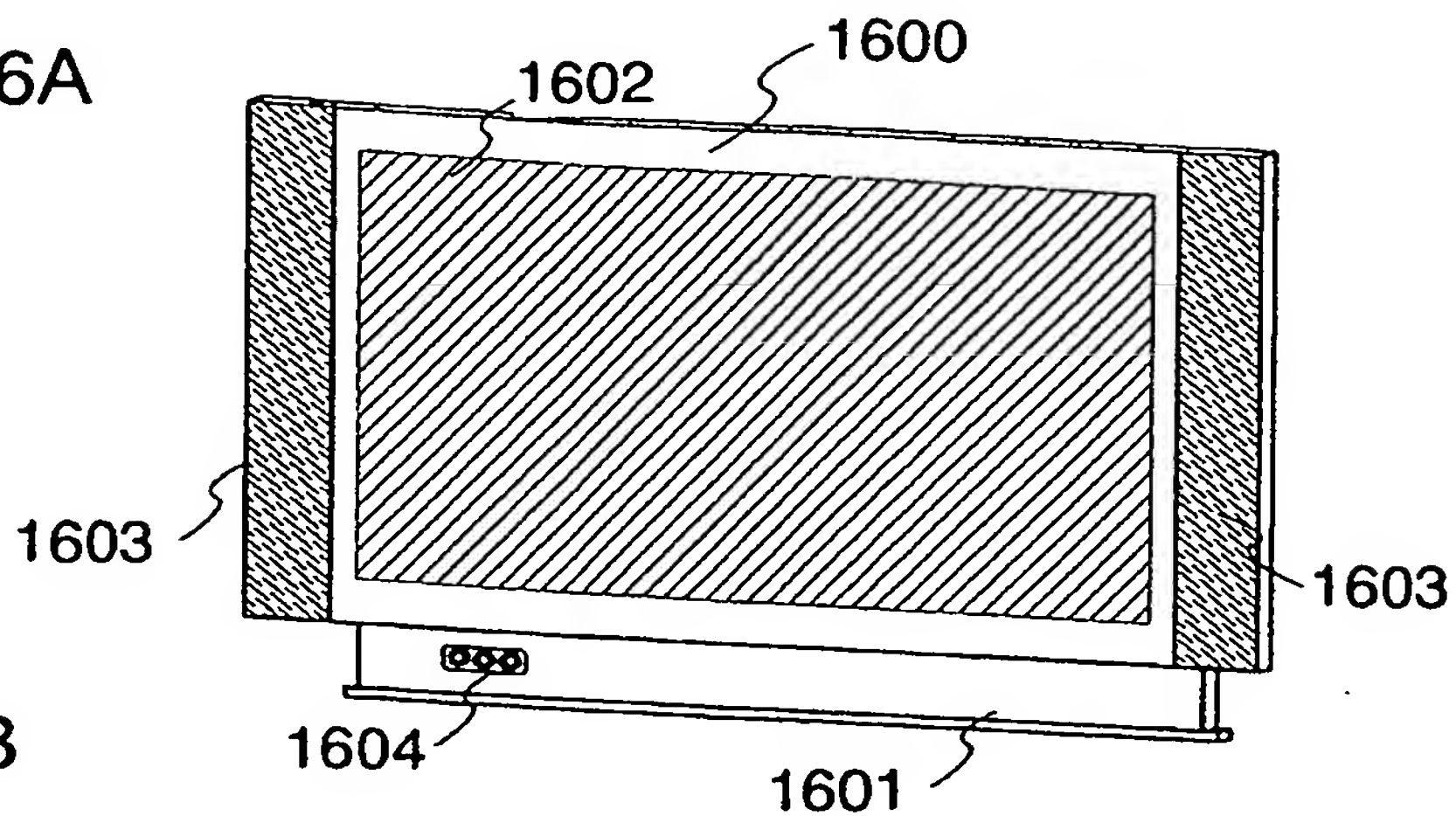


FIG. 36B

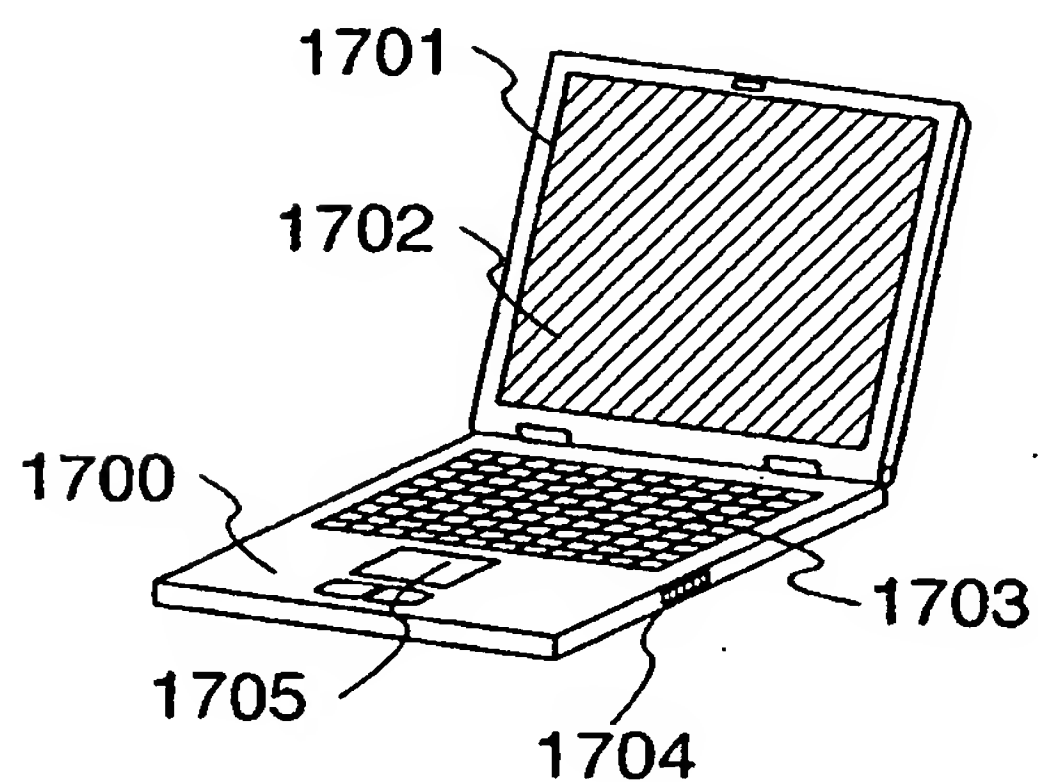


FIG. 36C

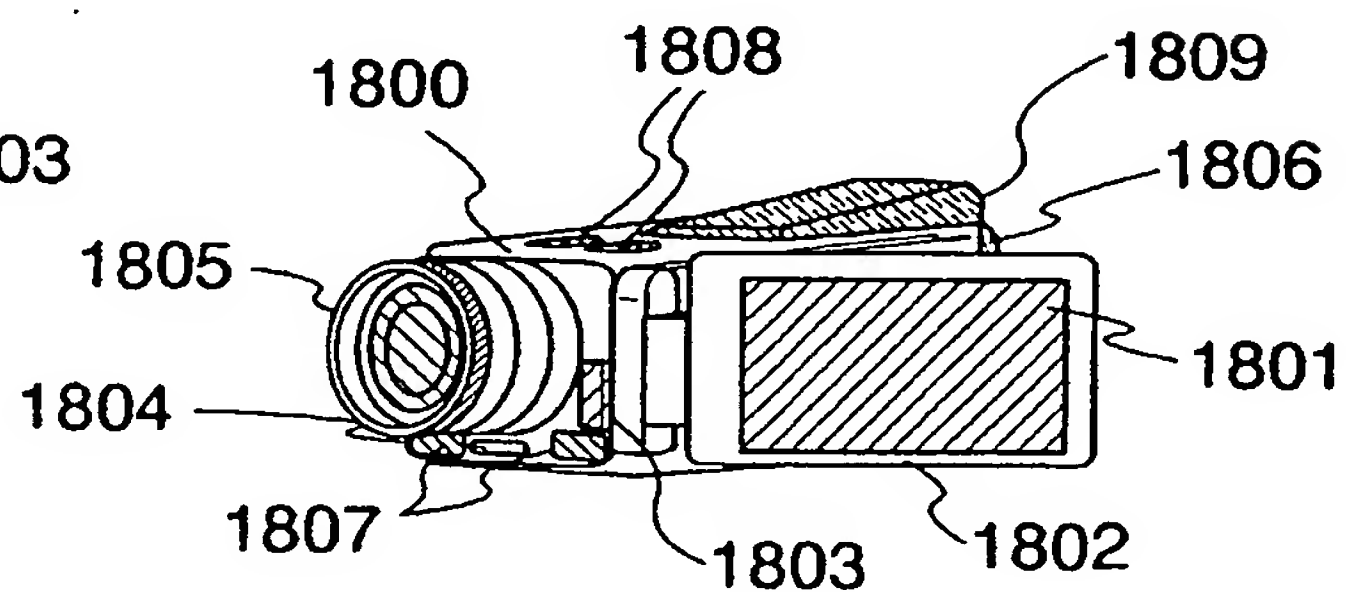


FIG. 36D

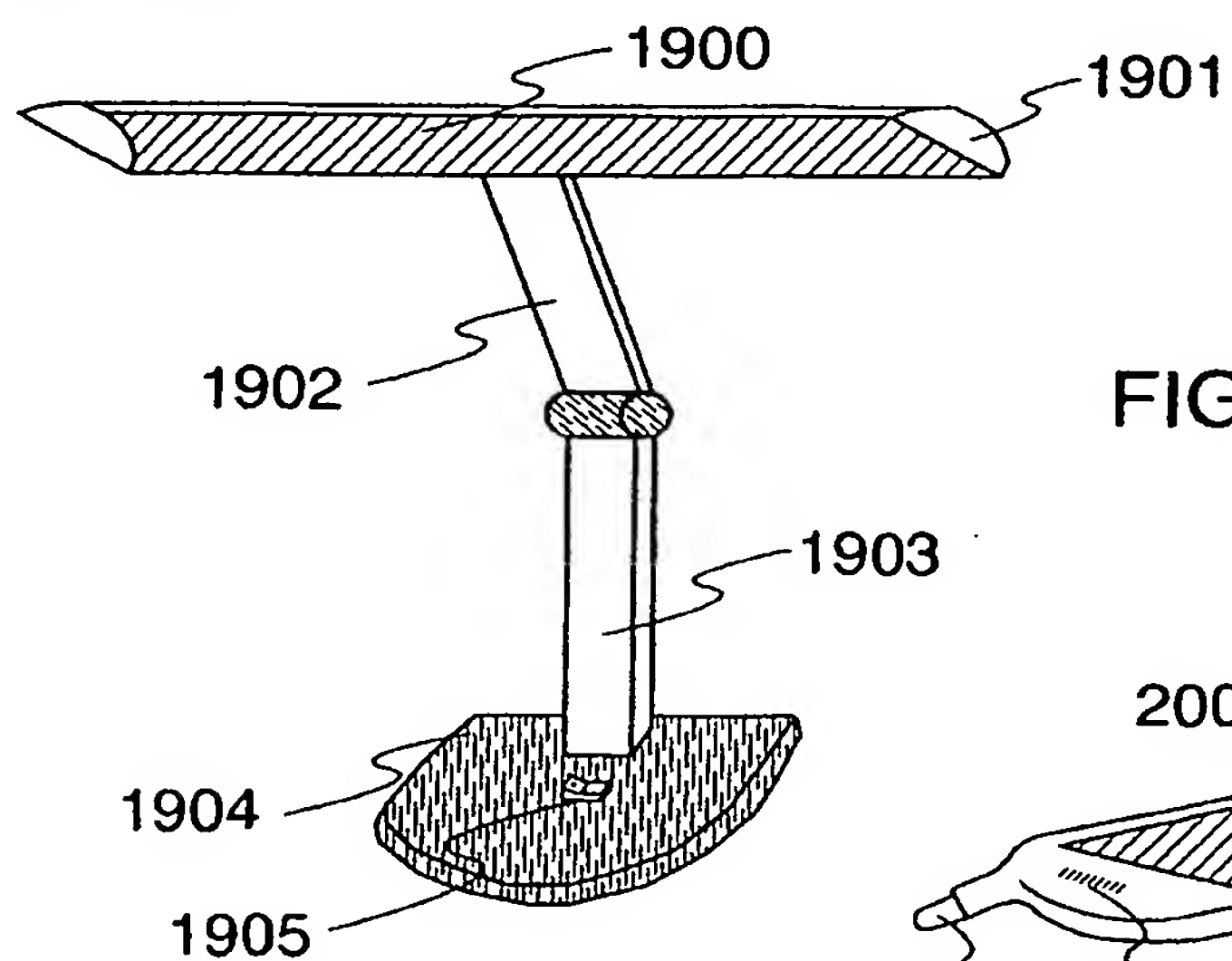
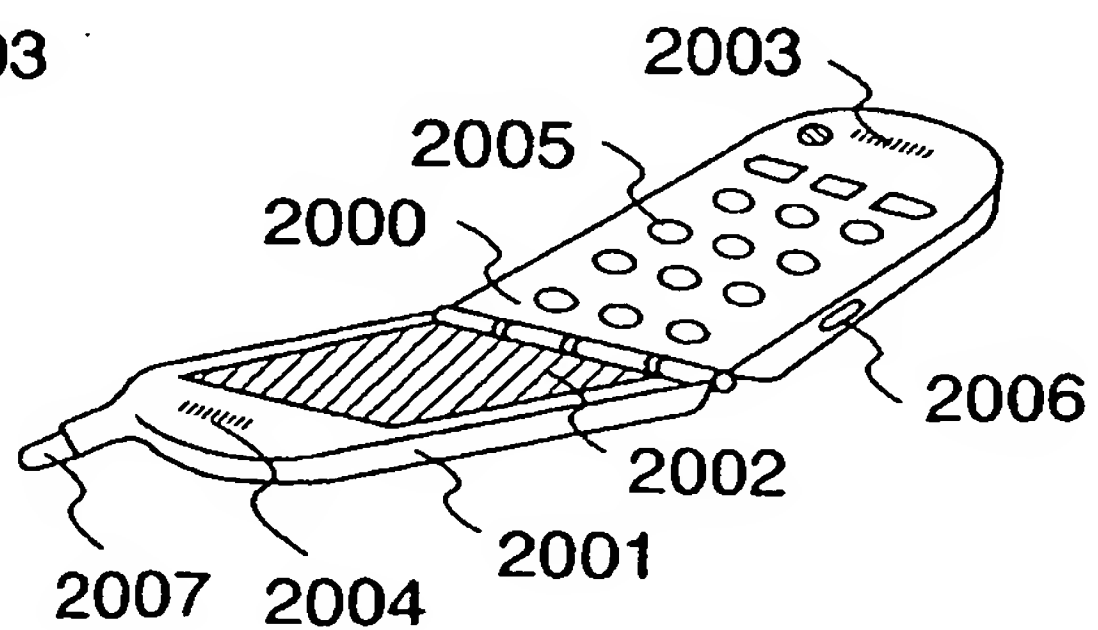


FIG. 36E



37/48

FIG. 37

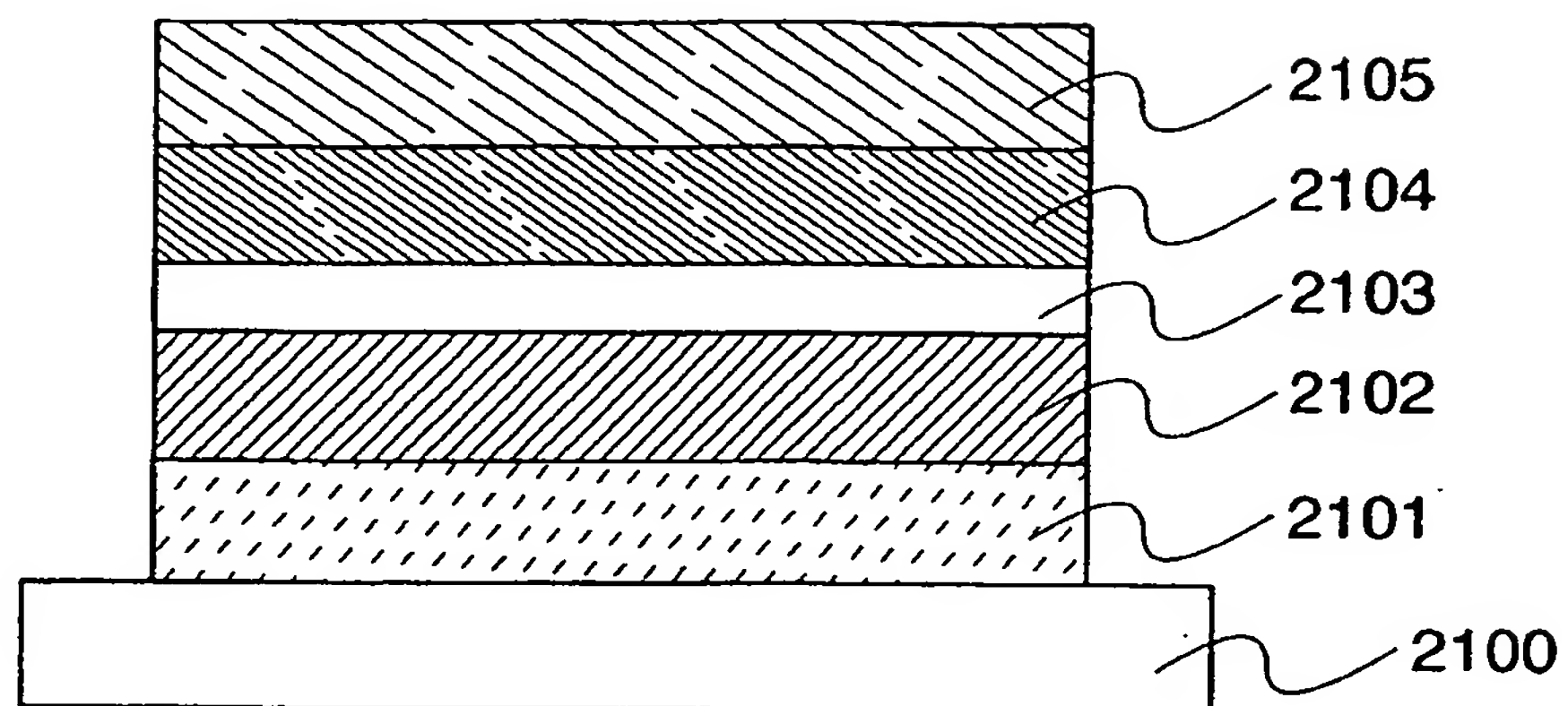


FIG. 38

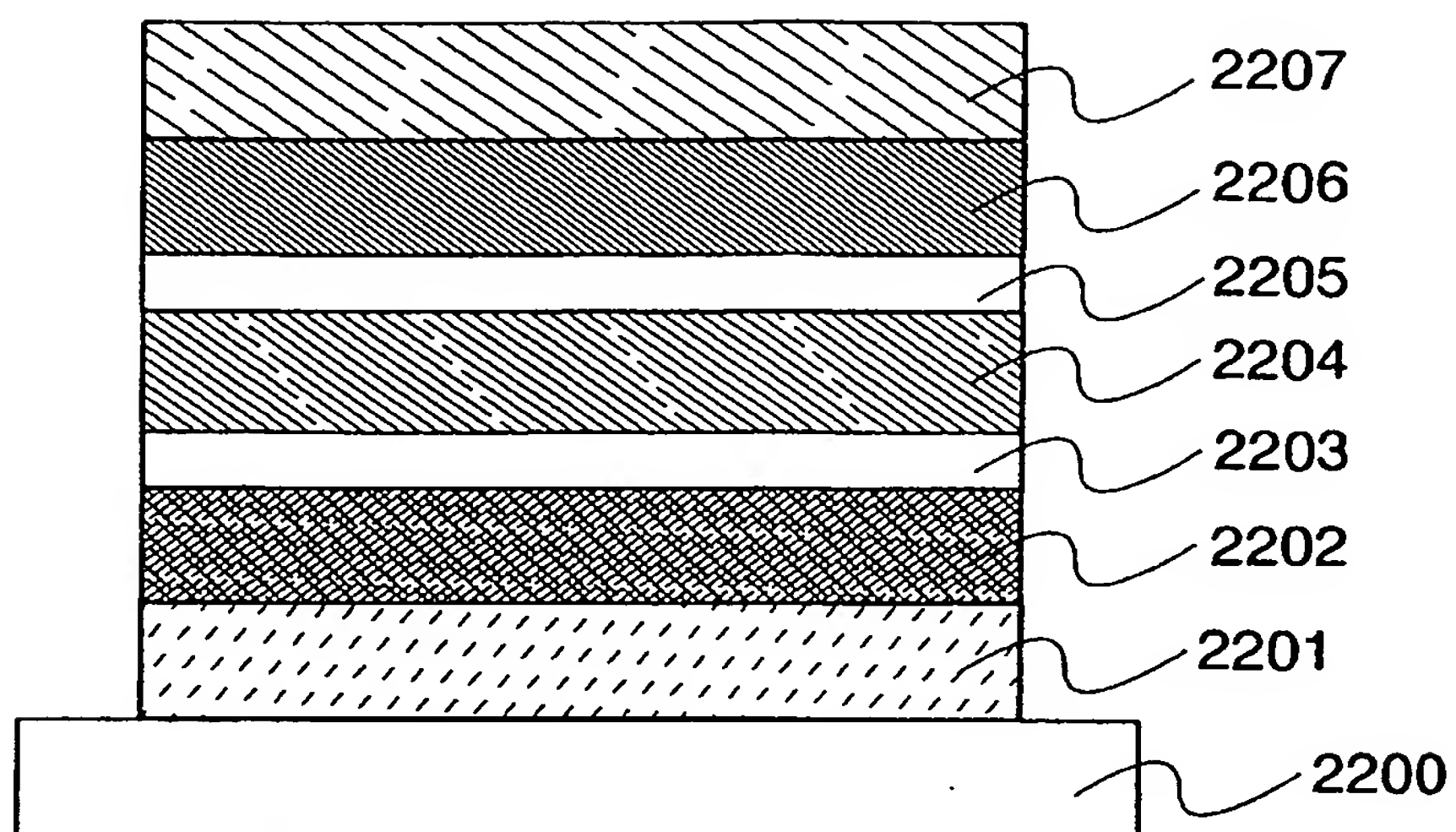
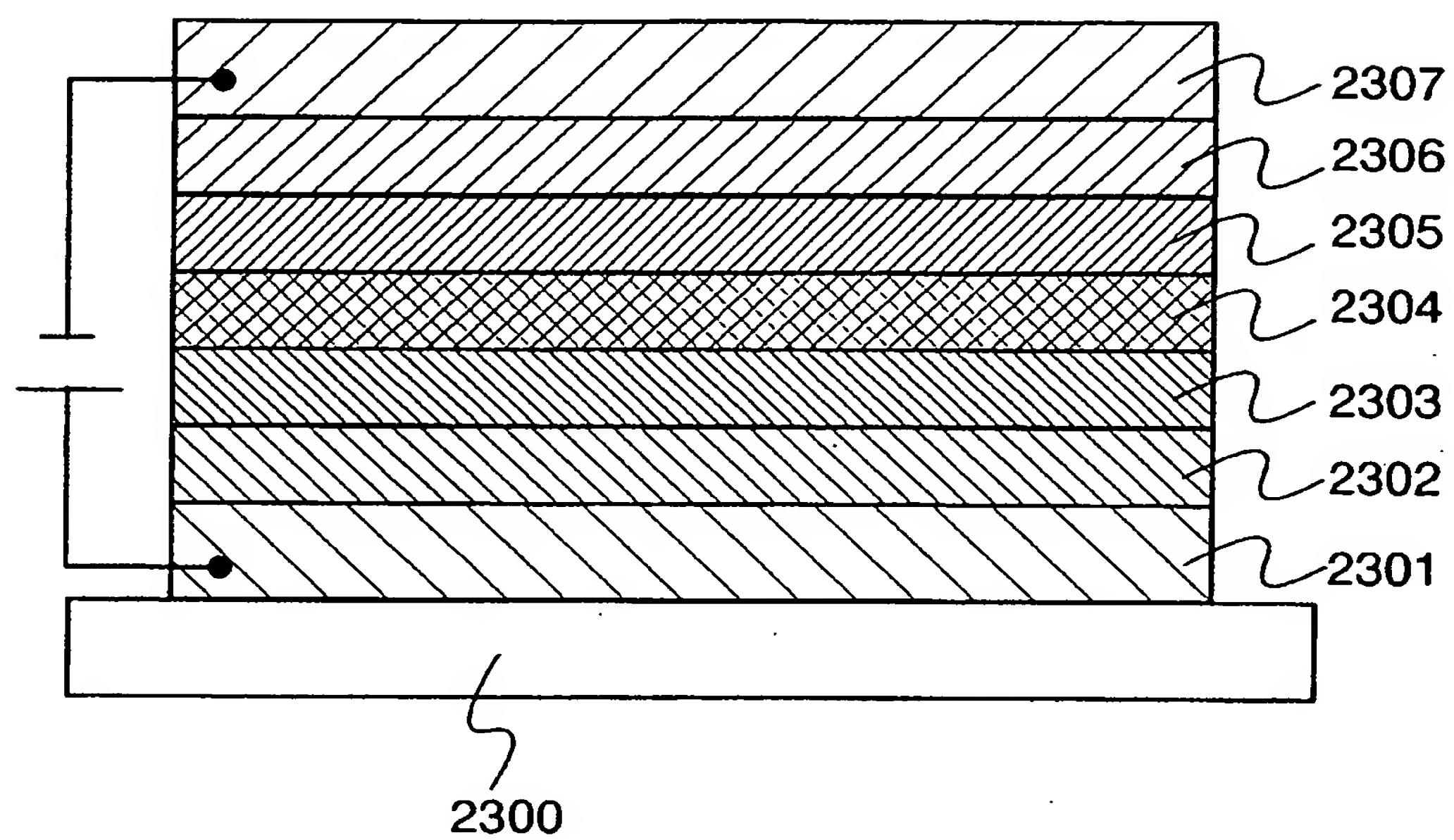


FIG. 39



40/48

FIG. 40

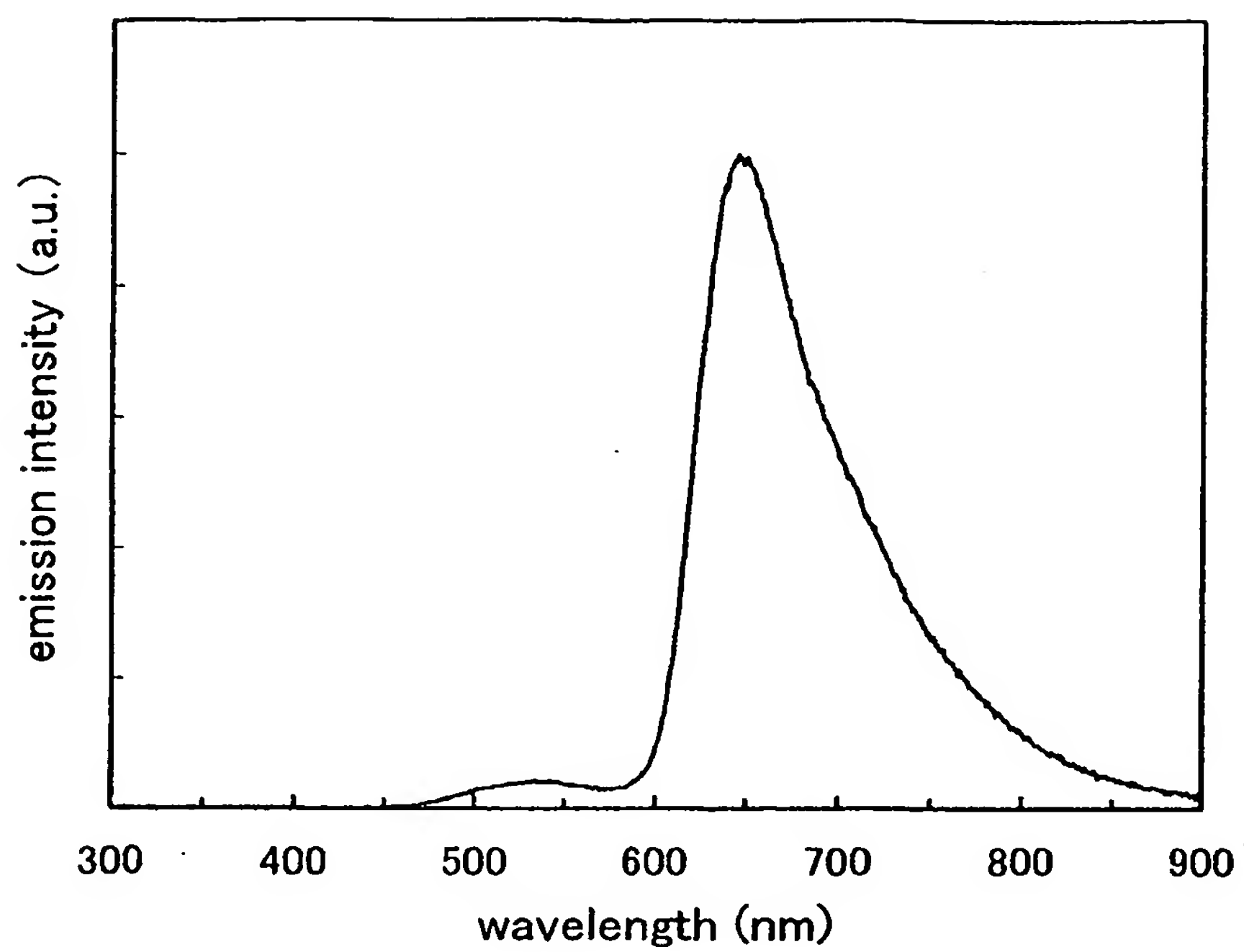


FIG. 41

41/48

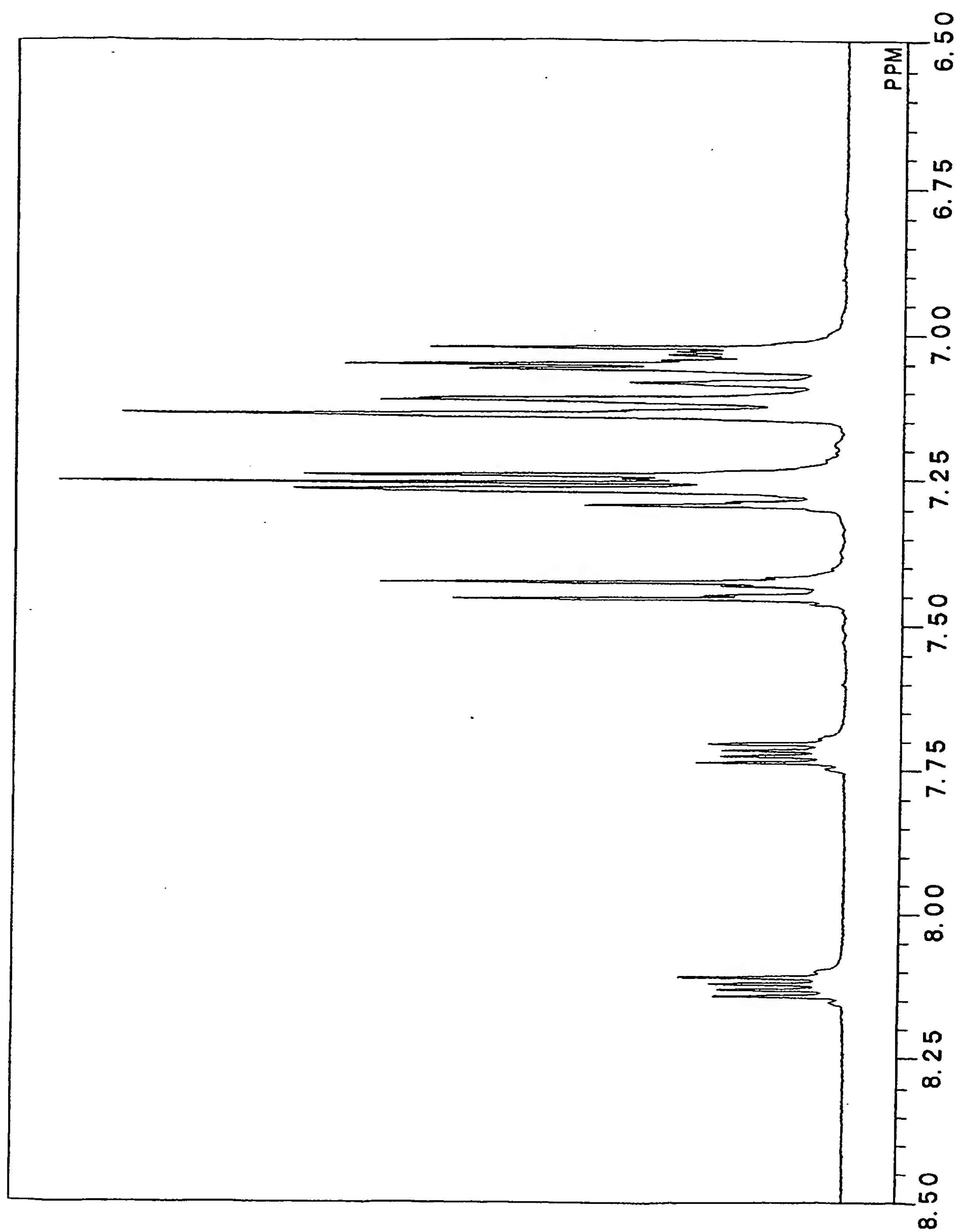
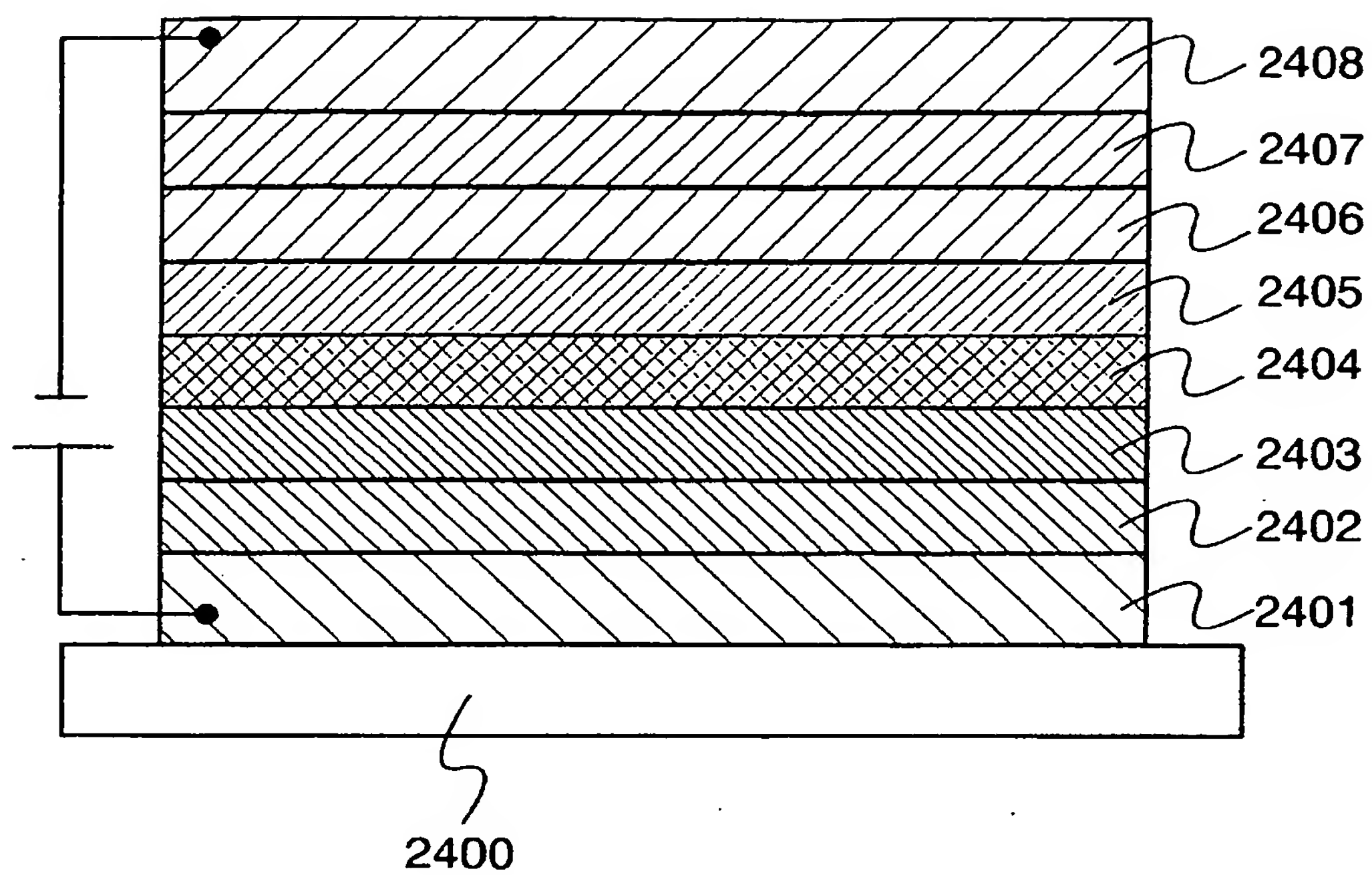


FIG. 42



43/48

FIG. 43

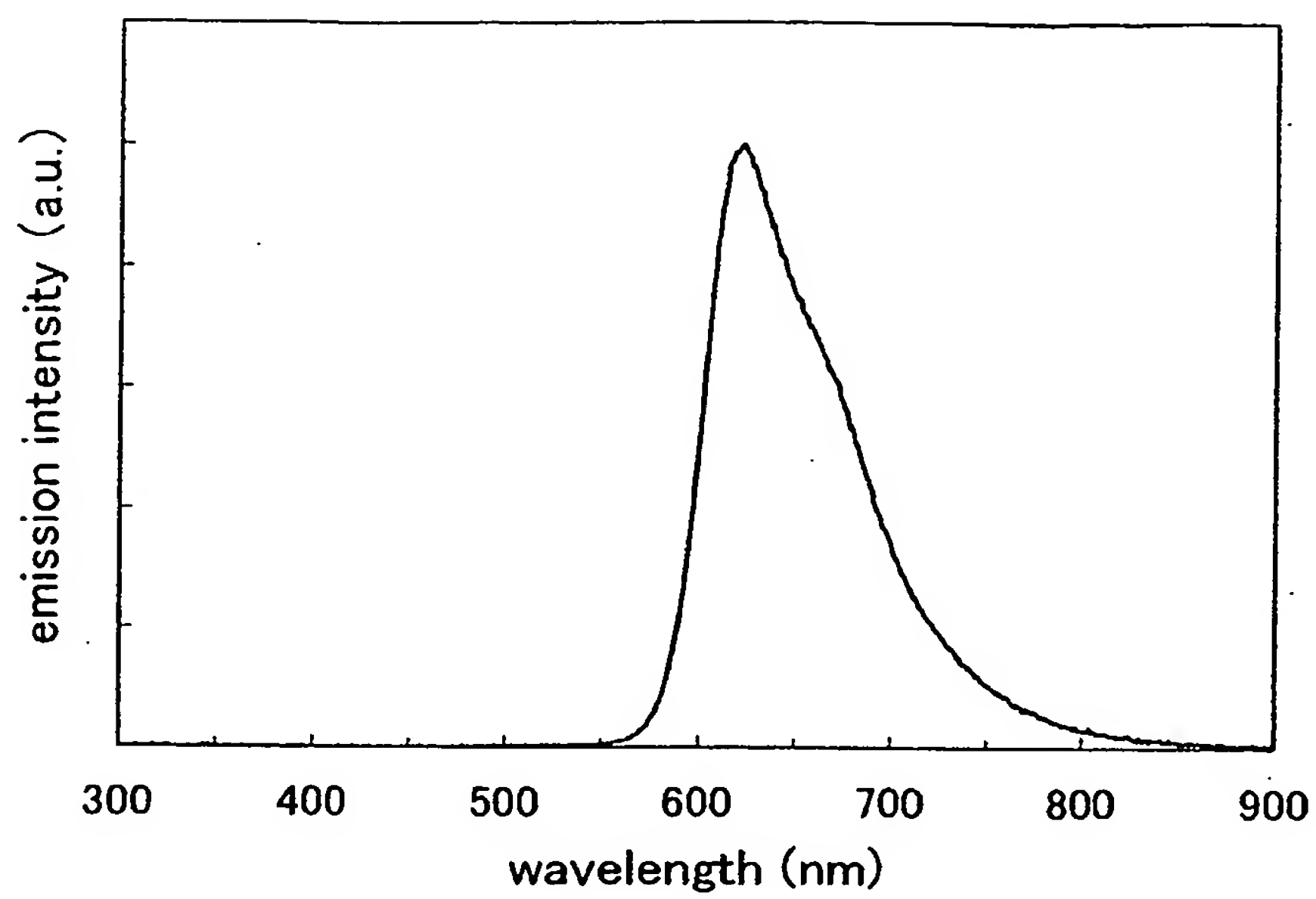
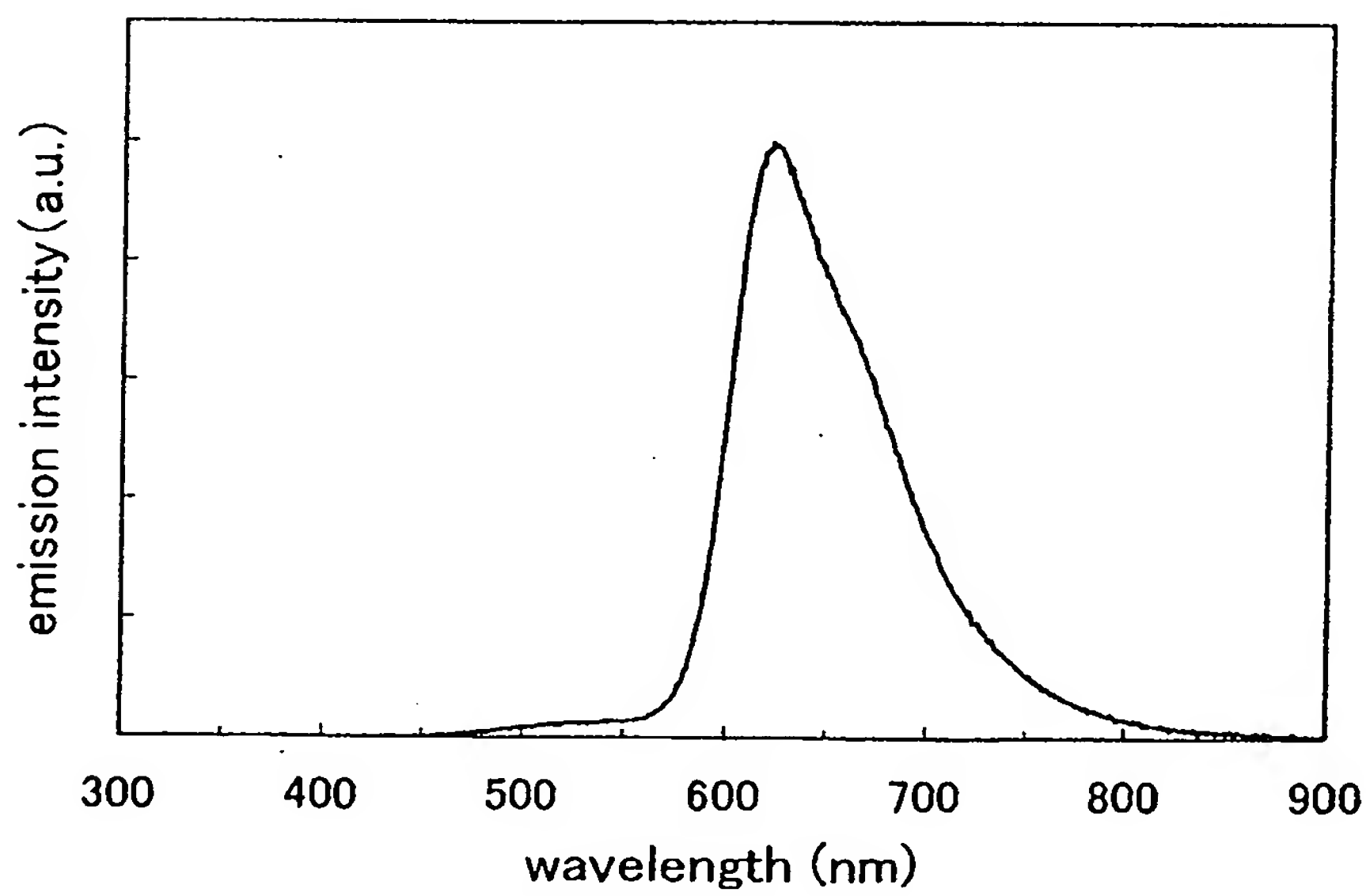
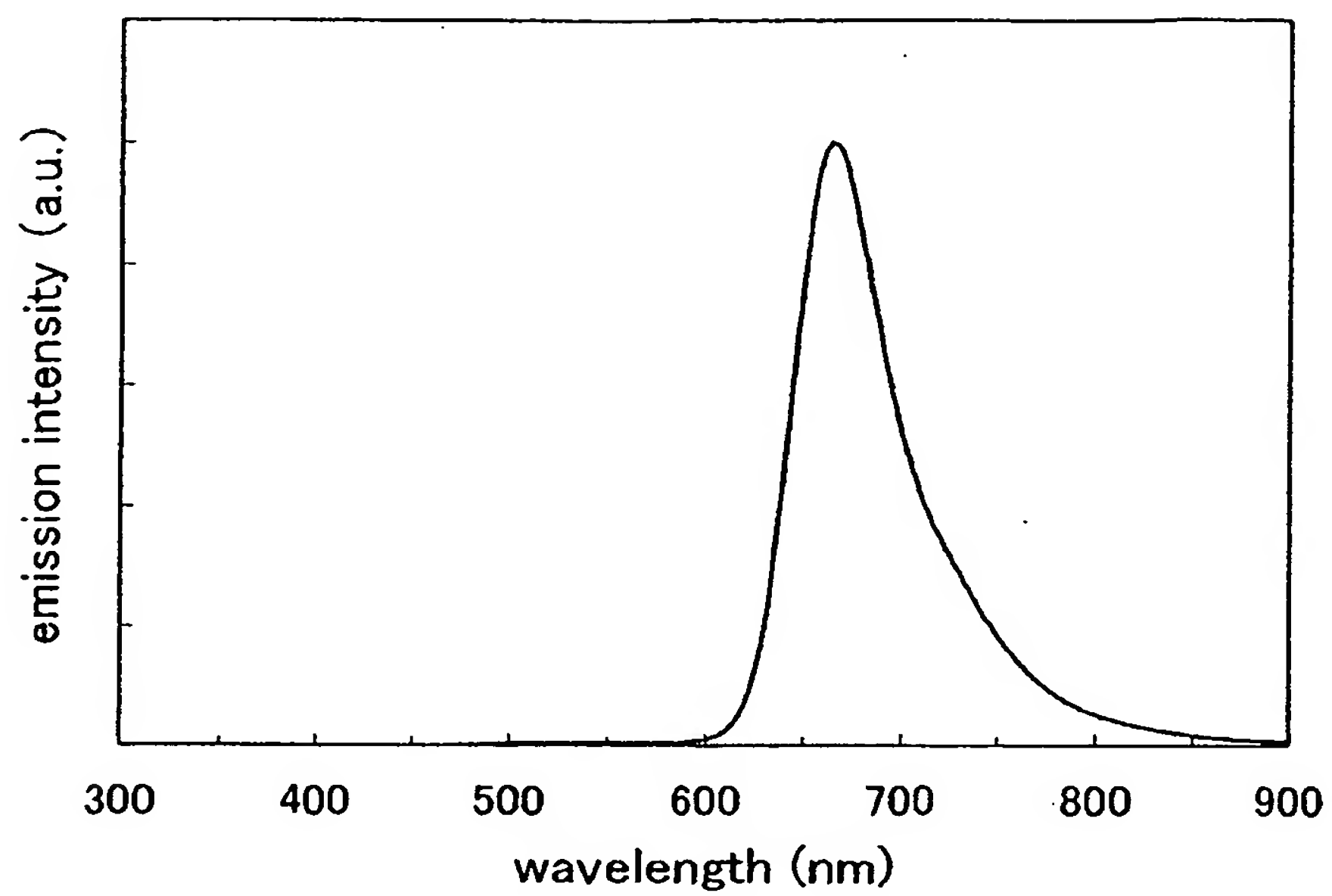


FIG. 44



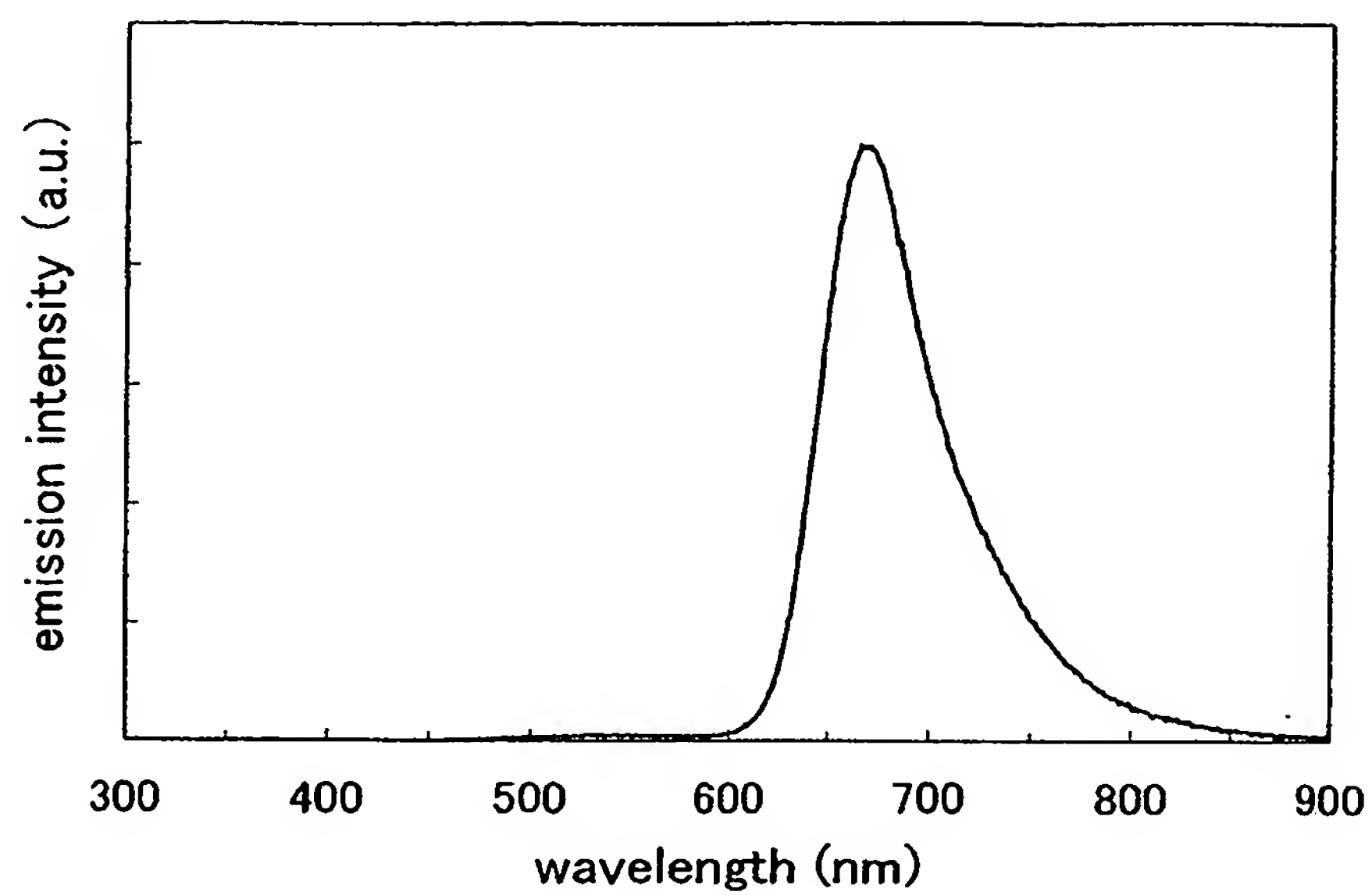
44/48

FIG. 45



45/48

FIG. 46



EXPLANATION OF REFERENCE

100: substrate, 101: first electrode, 102: layer including luminescent material, 103:
second electrode, 111: hole injecting layer, 112: hole transporting layer, 113:
5 light-emitting layer, 114: hole blocking layer, 115: electron transporting layer, 200:
substrate, 201: first electrode, 202: layer including luminescent material, 203: second
electrode, 211: electron transporting layer, 212: hole blocking layer, 213: light-emitting
layer, 214: hole transporting layer, 215: hole injecting layer, 300: substrate, 311: TFT,
312: TFT, 313: light-emitting element, 314: first electrode, 315: layer including
10 luminescent material, 316: second electrode, 317: wiring, 401: first electrode, 402:
second electrode, 411: hole injecting layer, 412: hole transporting layer, 413:
light-emitting layer, 414: electron transporting layer, 415: electron injecting layer, 501:
first electrode, 502: second electrode, 511: electron injecting layer, 512: electron
transporting layer, 513: first light-emitting layer, 514: partition layer, 515: second
15 light-emitting layer, 516: hole transporting layer, 517: hole injecting layer, 601: first
electrode, 602: second electrode, 611: electron injecting layer, 612: electron transporting
layer, 613: first light-emitting layer, 614: hole transporting layer, 615: first layer (hole
generation layer), 616: second layer (electron generation layer), 617: electron
transporting layer, 618: second light-emitting layer, 619: hole transporting layer, 620:
20 hole injecting layer, 701: first electrode, 702: second electrode, 711: hole injecting layer,
712: hole transporting layer, 713: light-emitting layer, 714: electron transporting layer,
715: electron injecting layer, 800: substrate, 801: FPC (flexible printed circuit), 802:
PWB (printed wiring board), 811: pixel portion, 812: source signal line driver circuit,
813: writing gate signal line driver circuit, 814: erasing gate signal line driver circuit,
25 901: first transistor, 902: second transistor, 903: light-emitting element, 911: gate signal
line, 912: source signal line, 913: writing gate signal line driver circuit, 914: erasing
gate signal line driver circuit, 915: source signal line driver circuit, 916: power source,
917: current supply line, 918: switch, 919: switch, 920: switch, 1001: first transistor,
1002: second transistor, 1003: gate signal line, 1004: source signal line, 1005: current
30 supply line, 1006: power source, 1101a: writing period, 1102a: writing period, 1103a:

writing period, 1104a: writing period, 1101b: retention period, 1102b: retention period, 1103b: retention period, 1104b: retention period, 1101: first sub-frame, 1102: second sub-frame, 1103: third sub-frame, 1104: fourth sub-frame, 1210: substrate, 1211: transistor, 1212: light-emitting element, 1213: first electrode, 1214: second electrode, 1215: layer in which hole generation layer, electron generation layer, and layer including luminescent material are stacked, 1216 (1216a and 1216b): first interlayer insulating film, 1216c: silicon nitride film including argon (Ar), 1217: wiring, 1218: partition layer, 1219 (1219a and 1219b): second interlayer insulating film, 1300: substrate, 1301: first electrode (anode), 1302: layer including luminescent material, 1303: second electrode (cathode), 1311: hole injecting layer, 1312 hole transporting layer, 1313: light-emitting layer, 1314: electron transporting layer, 1315: electron injecting layer, 1400: substrate, 1401: first electrode (anode), 1402: layer including luminescent material, 1403: second electrode (cathode), 1411: hole injecting layer, 1412 hole transporting layer, 1413: light-emitting layer, 1414: electron transporting layer, 1415: electron injecting layer, 1501: driver circuit portion (source side driver circuit), 1502: pixel portion, 1503: driver circuit portion (gate side driver circuit), 1504: sealing substrate, 1505: sealing material, 1506: inside surrounded by sealing material 1505, 1507: wiring, 1508: FPC to serve as external input terminal, 1509: substrate, 1510: switching TFT, 1511: current controlling TFT, 1512: first electrode, 1513: insulator, 1514: layer including luminescent material, 1515: second electrode, 1516: light-emitting element, 1517: n-channel TFT, 1518: p-channel TFT, 1600: frame body, 1601: support, 1602: display portion, 1603: speaker portion, 1604: video input terminal, 1700: main body, 1701: frame body, 1702: display portion, 1703: keyboard, 1704: external connection port, 1705: pointing mouse, 1800: main body, 1801: display portion, 1802: frame body, 1803: external connection port, 1804: remote-control receiving portion, 1805: image receiving portion, 1806: battery, 1807: sound input portion, 1808: operation key, 1809: eye piece, 1900: lighting portion, 1901: shade, 1902: variable arm, 1903: support, 1904: pedestal, 1905: power source, 2000: main body, 2001: frame body, 2002: display portion, 2003: sound input portion, 2004: sound output portion, 2005: operation key, 2006: external connection port, 2007: antenna, 2100: substrate, 2101:

first electrode, 2102: first light-emitting region, 2103: separation layer, 2104: second
light-emitting region, 2105: second electrode, 2200: substrate, 2201: first electrode,
2202: first light-emitting region, 2203: carrier generation layer, 2204: second
light-emitting region, 2205: carrier generation layer, 2206: third light-emitting region,
5 2207: second electrode, 2300: substrate, 2301: first electrode, 2302: hole injecting layer,
2303: hole transporting layer, 2304: light-emitting layer, 2305: electron transporting
layer, 2306: electron injecting layer, 2307: second electrode, 2400: substrate, 2401: first
electrode, 2402: hole injecting layer, 2403: hole transporting layer, 2404: light-emitting
layer, 2405: hole blocking layer, 2406: electron transporting layer, 2407: electron
10 injecting layer, 2408: second electrode

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/009310

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ H05B33/14, C09K11/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ H05B33/14, C09K11/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2005
 Registered utility model specifications of Japan 1996-2005
 Published registered utility model applications of Japan 1994-2005

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA (STN), REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2002/045466 A1 (Canon Kabushiki Kaisha) 2002.06.06 & US 2003/0059646 A1 & US 2003/0068526 A1 & EP 1349435 A1 & EP 1348711 A1	1-33
A	P.J.STEEL and G.B.CAYGILL, Cyclometallated compounds. Double cyclopalladation of diphenyl pyrazines and related ligands, Journal of Organometallic Chemistry, 395, 1990, P.359-373	1-33

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

09.08.2005

Date of mailing of the international search report

30.8.2005

Name and mailing address of the ISA/JP

Japan Patent Office

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Authorized officer

YOKO WATANABE

Telephone No. +81-3-3581-1101 Ext. 3483

4V 9279

ELECTROPHOTOGRAPHIC POSITIVE CHARGE SENSITIVE BODY AND ITS IMAGE FORMING PROCESS

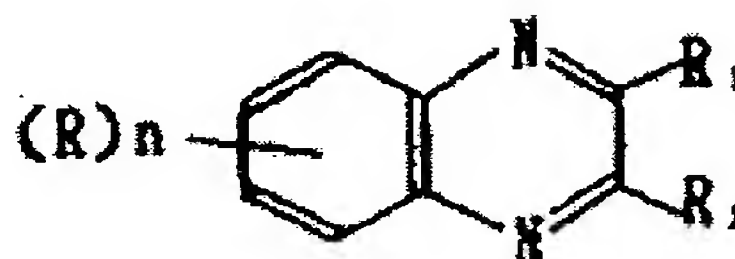
Patent number: JP63159856
Publication date: 1988-07-02
Inventor: TAMAKI KIYOSHI; KUDO KOICHI; ETO YOSHIHIKO; TAKEI YOSHIAKI
Applicant: KONISHIROKU PHOTO IND
Classification:
- international: G03G5/05; G03G5/06; G03G5/05; G03G5/06; (IPC1-7): G03G5/05
- european: G03G5/05A4F; G03G5/06D2F4
Application number: JP19860309690 19861224
Priority number(s): JP19860309690 19861224

Report a data error here

Abstract of JP63159856

PURPOSE: To improve the UV ray resisting property, the durability and the sensitivity of the titled body by incorporating a specific compd. to the electrophotographic sensitive body.

CONSTITUTION: The electrophotographic sensitive body comprises the positive charge photosensitive body layer which contains an electric charge generating substance (CGM) and an electric charge transfer substance (CTM) is provided on a conductive substrate body. The titled body contains the compd. shown by formula wherein R₁ and R₂ are each hydrogen atom, alkyl or aryl group, R is hydrogen or halogen atom, nitro, amino, alkyl, alkoxy, aryl, or aralkyl group, (n) is 0, 1 or 2, when (n)=2, R may be the same or the different with each other. The photosensitive body layer provided on the substrate body may be composed of a monolayer structure formed by mixing CTM and CGM or a plural layer structure formed by laminating a layer contg. CTM as an lower layer and a layer contg. CGM as an upper layer. If necessary, a protective layer may be provided on the titled body. Said compd. is incorporated to any one layer of the photosensitive body layer, but, said compd. is preferably incorporated to the surface layer of the photosensitive body layer.



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⑭ 発明の名称 電子写真正帯電感光体及びその像形成プロセス
⑮ 特 願 昭61-309690
⑯ 出 願 昭61(1986)12月24日
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明 細 書

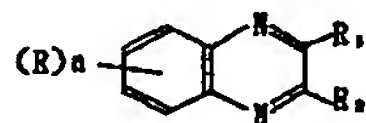
1. 発明の名称

電子写真正帯電感光体及びその像形成プロセス

2. 特許請求の範囲

(1) 導電性支持体上に電荷輸送物質及び電荷発生物質を含んでなる層を有する電子写真感光体に於て、下記一般式で表される化合物を含有することを特徴とする電子写真正帯電感光体。

一般式



(式中、R₁及びR₂は水素原子またはアルキル、アリール基を表す。Rは水素原子、ハロゲン原子またはニトロ、アミノ、アルキル、アルコキシ、アリール、アラルキルの各置換基を表し、nは0、1または2である。n=2の時Rは同じでも異っていてもよい。)

(2) 前記電子写真正帯電感光体に於て、導電性支持体上に電荷輸送層、電荷発生層及び必要に応じて設けられる保護層の順に積層し、電荷発

生層中に電荷輸送物質を含有し、且つ電荷発生層及び／または必要に応じて設けられる保護層に前記一般式で示される化合物を含有することを特徴とする特許請求の範囲第1項記載の電子写真正帯電感光体。

(3) 前記電子写真正帯電感光体を用いて、該感光体上に正電荷を付与し、像露光を行って正の静電潜像を形成し、トナー現像を施すことを特徴とする像形成プロセス。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は電子写真感光体に関し、特に正帯電用感光体に関する。

(従来の技術)

従来、例えば電子写真感光体としては、セレン、酸化亜鉛、硫化カドミウム等の無機光導電性物質を含有する感光層を有する感光体が広く用いられている。

一方、種々の有機光導電性物質を電子写真感光体の感光体層の材料として利用することが近年活

発に研究、開発されている。

例えば特公昭50-10496号には、ポリ－β－ビニルカルバゾールと2,4,7-トリニトロ－9-フルオレノンを含む感光体層を有する有機感光体について記載されている。しかしこの感光体は、感度及び耐久性において必ずしも満足できるものではない。このような欠点を改善するために、感光体層において、電荷発生物質と電荷輸送機能とを異なる物質に個別に分担させることにより、感度が高く耐久性の大きい有機感光体を開発する試みがなされている。このような、いわば機能分離型の電子写真感光体においては、各機能を発揮する物質を広い範囲のものから選択することができるので、任意の特性を有する電子写真感光体を比較的容易に作製することが可能である。

、こうした機能分離型の電子写真感光体に有効な電荷発生物質として、従来数多くの物質が提案されている。無機物質を用いる例としては、例えば特公昭43-18198号に記載されているように、無定形セレンがあり、これは有機電荷輸送物質と組合

成する際、感光体表面の正電荷を能率よく打消すため前記電荷輸送層に電子輸送能の大きい、例えばトリニトロフルオレノン等が使用される。しかし該物質は発癌性があり、労働衛生上極めて不適当である等の問題を生ずる。

さらに正帯電感光体として、米国特許3,815,414号には、チアピリリウム塩(電荷発生物質)をポリカーボネート(バインダ樹脂)と共晶錯体を形成するように含有させたものが示されている。しかしこの公知の感光体では、メモリ現象が大きく、ゴーストも発生し易いという欠点がある。又米国特許3,357,989号にも、フクロシアニンを含む感光体を示されているが、フクロシアニンは結晶型によって特性が変化する上に、結晶型を厳密に制御しなければならないという難点があり、かつメモリ現象が大きく、短波長感度が低いため前記短波長を含む可視光を光源とする複写機には不適当である。

このように正帯電用感光体を得るための試みが種々行なわれているが、いずれも光感度、メモリ

される。

また、有機染料や有機顔料を電荷発生物質として用いた電子写真感光体も多数提案されており、例えば、ビスアゾ化合物を含む感光体層を有するものは、特開昭47-37543号、同55-22834号、同54-79832号、同56-116040号等により既に知られている。尚これらの有機光導電性物質は通常負帯電感光体で使用されていて、その理由は、負帯電使用の場合には、電荷のうちホールの移動度が大きいことから、光感度等の面で有利なためである。しかしながら、このような負帯電使用では、帯電器による負帯電時に雰囲気中にオゾンが発生し易くなり、環境条件を悪くするという問題がある。さらに他の問題は、負帯電用感光体の現像には正極性のトナーが必要となるが、正極性のトナーは強磁性体電荷粒子に対する摩擦帯電系列からみて製造が困難であることである。

そこで、有機光導電性物質を用いる感光体を正帯電で使用することが提案されている。例えば、電荷発生層上に電荷輸送層を積層して感光体を形

現象又は労働衛生等の点で改善すべき多くの問題点がある。

そこで光照射時ホール及び電子を発生する電荷発生物質を含む電荷発生層を上層(表面層)とし、ホール輸送機能を有する電荷輸送物質を含む電荷輸送層を下層とする積層構成の感光体層を有する感光体を正帯電用として使用することが考えられる。さらに又、前記電荷発生物質と前記電荷輸送物質を含む単層構成の感光体層を有する感光体も正帯電用として使用可能と考えられる。

なおかかる正帯電用とされる感光体においては、構造中に例えば電子吸引性基を有する電荷発生物質を用いるようにすれば、感光体表面の正電荷を打消すための電子の移動が早くなり、高感度特性が得られることが考えられる。

しかしながら、前記正帯電用感光体はいずれも電荷発生物質を含む層が表面層として形成されるため、光照射時に紫外線等の短波光照射、コロナ放電、湿度、機械的摩擦等の外部作用に脆弱な電荷発生物質が前記表面層近傍に存在することとな

り、感光体の保存中及び像形成の過程で電子写真性能が劣化し、画質が低下するようになる。

従来の電荷輸送層を表面層とする負帯電用感光体においては、前記各種の各部作用の影響は極めて少なく、むしろ前記電荷輸送層が下層の電荷発生層を保護する作用を有している。

そこで、例えば絶縁性かつ透明な樹脂から成る薄い保護層を設け、前記電荷発生物質を含む層を外部作用から保護することが考えられるが、光照射時発生する電荷が該保護層でブロッキングされて光照射効果が失なわれてくるし、また表面層となる保護層の膜厚が厚い場合には感度低下を招き、利え紫外線遮断効果も少いので、外部作用からの遮蔽、特に紫外線からの保護を単なる保護層だけに委ねることはできない。

〔発明の目的〕

本発明の目的は、電荷発生物質(CGMと標記)及び電荷輸送物質(CTMと標記)を含んでなり正帯電性感光体層を有し、紫外線耐性のよい高感度で耐久性の大きい電子写真正帯電感光体を提供す

ることにあり、本発明に係る化合物は前記の少くとも一層に添加されるが感光体層表面に添加されることが好ましい。尚表面に最も濃密に、内部にゆくに従って遞減させる形態であってもよい。

以下に本発明を詳しく説明する。

カールソンプロセスに基づく電子写真プロセスには、一般に像露光、消去露光、転写前露光、クリーニング露光等に紫外線を発生する光源が用いられており、該光源からの光に含まれ、可視光に比べ大きなエネルギーを有する紫外線の繰返し照射は、感光体に用いられている有機化合物分子を解裂させるに充分である。即ち感光体をなすCGM、CTM或はバインダ等はラジカル解離を起し本来の分子構造を失って劣化し、従って感光体の劣化を招来し、具体的には感度低下、残電位上昇等を惹起し、かぶりの発生、画質の低下に陥る。

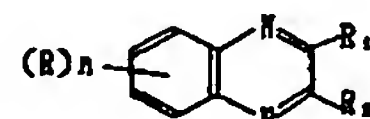
従来の技術でも記述したように有機光導電性物質を用いた正帯電用感光体においては、電荷発生層(以下、CGLと標記)が表面層となるので耐傷性に欠け、耐久性向上のためにはCGL膜厚を厚

くすることにある。

〔発明の構成および作用効果〕

前記した本発明の目的は、導電性支持体上にCTM及びCGMを含んでなる層を有する電子写真感光体に於て、下記一般式で表される化合物を含有することを特徴とする電子写真正帯電感光体によって達成される。

一般式



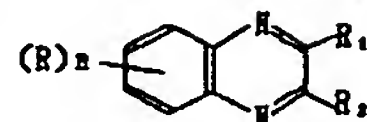
式中、R₁及びR₂は水素原子またはアルキル、アリール基を表す。Rは水素原子、ハロゲン原子またはニトロ、アミノ、アルキル、アルコキシ、アリール、アラルキルの各置換基を表し、nは0、1または2である。n=2の時Rは同じでも異っていてもよい。

本発明に係る導電性支持体上に設ける感光体層は、CTM及びCGMを混和した単層構成でもよいし、CTMを含む層を下層としCGMを含む層を上層とする複層構成でもよい。また必要に応じて保護層(OCILと標記)を設けてもよい。

くする必要がある。しかしながら、膜厚を厚くすると感度低下を引起す。この感度低下を抑制する手段としてCGL中への電荷輸送物質(CTM)の添加が効果的であるが、このCTMは電荷発生物質(CGM)に比べ紫外線酸化を受け易い構造を有するので、紫外線により容易に劣化され感光体の耐久性が損われてしまう。

本発明者らは、紫外線劣化防止に関し鋭意検討の結果、正帯電感光体の表面層であるCGL中にイミダゾリン類化合物を含有させることにより、上記劣化を著しく軽減できることを見出した。前記した化合物即ち紫外線吸収剤の有機化合物安定化機構としては、紫外線(UVと標記することがある)の保有する分解エネルギーがUV吸収剤内で振動のエネルギーに変化することによると思われる。この振動のエネルギーは熱エネルギーとして該UV吸収剤から放出されるが、熱エネルギーは既に有機化合物を劣化させるには不十分であって、感光体が紫外線繰返し照射の害から保護されるものと思われる。

次に具体的化合物を例示する。



尚表中の接頭数字は置換位置を示す。

No	R_1	R_2	R_3
(1)	$-\text{CH}_3$		H
(2)	$-\text{C}_2\text{H}_5$		H
(3)			H
(4)	$-\text{OH}$		$\delta\text{-Cl}$
(5)	$-\text{C}_2\text{H}_5$		H
(6)	$-\text{C}_2\text{H}_5$		$\delta\text{-Br}$
(7)			H
(8)			$\delta\text{-Cl}$
(9)	$-\text{C}_2\text{H}_5$		H
(10)	$-\text{C}_2\text{H}_5$		H

に中間層が設けられてもよい。

次に本発明に通ずるCGMとしては、可視光を吸収してフリー電荷を発生するものであれば、無機顔料及び有機顔料の何れをも用いることができる。無定形セレン、三方晶系セレン、セレン-砒素合金、セレン-テルル合金、硫化カドミウム、セレン化カドミウム、碲セレン化カドミウム、硫化水銀、酸化鉛、硫化鉛等の無機顔料の外、次の代表例で示されるような有機顔料が用いてもよい。

- (1) モノアゾ顔料、ポリアゾ顔料、金属錯塩アゾ顔料、ピラゾロンアゾ顔料、スチルベンアゾ及びチアゾールアゾ顔料等のアゾ系顔料
- (2) ベリレン酸無水物及びベリレン酸イミド等のベリレン系顔料
- (3) アントラキノン誘導体、アントアントロン誘導体、ジベンズピレンキノン誘導体、ピラントロン誘導体、ピオラントロン誘導体及びイソピオラントロン誘導体等のアントラキノン系又は多環キノン系顔料
- (4) インジゴ誘導体及びチオインジゴ誘導体等

本発明の化合物の添加量は、CGL中に用いられる場合、CGL中のCTMに対して0.1~100重量%、好ましくは1~50重量%、特に好ましくは5~25重量%である。また、OCL中に用いられる場合、OCL中のバインダ樹脂に対して0.1~100重量%、好ましくは1~50重量%である。

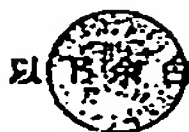
次に本発明の感光体の構成を図面によって説明する。感光体としては例えば第1図に示すように支持体1（導電性支持体またはシート上に導電層を設けたもの）上にCTMと必要に応じてバインダ樹脂を含有する電荷輸送層（CTLと表記）2を下層とし、CGM、CTMと必要に応じてバインダ樹脂を含有するCGL3を上層とする積層構成の感光体層4を設けたもの、第2図に示すように第1図の感光体層の上に保護層（OCL）4を設けたもの及び第3図に示すように支持体上にCGMとCTMと必要に応じてバインダ樹脂を含有する単層構成の感光体層4を設けたもの、等が挙げられるが、第3図の単層構成の感光体層上にOCLが設けられてもよく、また支持体と感光体層の間

のインジゴイド系顔料

- (5) 金属フタロシアニン及び無金属フタロシアニン等のフタロシアニン系顔料
- (6) ジフェニルメタン系顔料、トリフェニルメタン顔料、キサントン顔料及びアクリジン顔料等のカルボニウム系顔料
- (7) アジン顔料、オキサジン顔料及びチアジン顔料等のキノンイミン系顔料
- (8) シアニン顔料及びアゾメチン顔料等のメチン系顔料
- (9) キノリン系顔料
- (10) ニトロ系顔料
- (11) ニトロソ系顔料
- (12) ベンゾキノン及びナフトキノン系顔料
- (13) ナフタルイミド系顔料
- (14) ビスベンズイミダゾール誘導体等のベリノン系顔料

前記本発明に用いられるアゾ系顔料としては、例えば次の例示構造化合物群〔I〕~〔V〕で示されるものがあり、該例示構造化合物群の中の個

々の好ましい具体的化合物の数例を併せ掲げる。
その好ましい具体的化合物の全容については特
願昭61-195881号が参照される。



例示構造化合物群(Ⅰ):

X'-N=N-A'-N=N-X'		
化合物 NO	-A'-	-X'-
I-1		
I-2	"	
I-3		
I-4		

例示構造化合物群(Ⅱ):

X'-N=N-A'-N=N-A'-N=N-X'			
化合物NO	-A'-	-A'-	-X'-, -X''
II-1			
II-2	"	"	
II-3	"	"	
II-4	"	"	
II-5	"	"	
II-6	"	"	
II-7	"	"	

例示構造化合物群(Ⅲ):

X'-N=N-A'-N=N-A'-N=N-A'-N=N-X'				
化合物NO	-A'-	-A'-	-A'-	-X'-, -X''
III-1				
III-2	"	"	"	
III-3	"	"	"	
III-4	"	"	"	
III-5	"	"	"	
III-6	"	"	"	

例示構造化合物群〔Ⅳ〕:

化合物No	—A'—	—A''—	—X ^a —X ^b
Ⅳ-1			
Ⅳ-2	"	"	
Ⅳ-3	"	"	
Ⅳ-4	"	"	
Ⅳ-7	"		

例示構造化合物群〔Ⅴ〕:

化合物No	—X ^a —X ^b
V-1	
V-2	
V-3	
V-4	
V-5	

化合物No	—X ^a —X ^b
V-26	
V-27	
V-28	

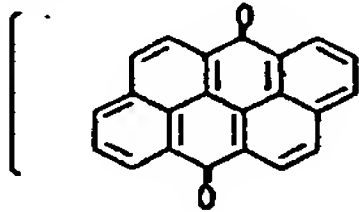
例示構造化合物群〔Ⅵ〕:

化合物名	R ¹	R ²	R ³	R ⁴	X ^{a,b}	n
Ⅵ-1	—	—	—	—	—	0
Ⅵ-2	Cl	Cl	—	—	—	0
Ⅵ-3	Br	Br	—	—	—	0
Ⅵ-4	—	—	Br	Br	—	0
Ⅵ-5	Br	Br	Br	Br	—	0
Ⅵ-6	—	—	—	—	I	2
Ⅵ-7	—	—	—	—	"	3
Ⅵ-8	—	—	—	—	"	4
Ⅵ-9	—	—	—	—	NO ₂	2
Ⅵ-10	—	—	—	—	CS	2
Ⅵ-11	—	—	—	—	COCH ₃	2

また、以下の多環キノン顔料から成る例示構造化合物群〔Ⅵ〕～〔Ⅺ〕はCGMとして最も好ましく使用できる。

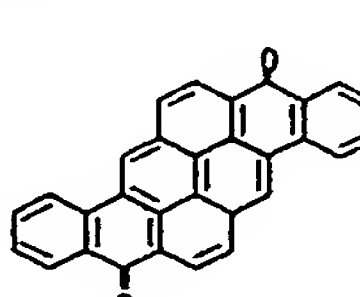
以下余白

例示構造化合物群〔Ⅶ〕:

		
化合物No	X''	n
Ⅶ-1	—	0
Ⅶ-2	Cl	2
Ⅶ-3	Br	2
Ⅶ-4	I	2
Ⅶ-5	I	3
Ⅶ-6	I	4
Ⅶ-7	NO ₂	2
Ⅶ-8	CN	2
Ⅶ-9	COC ₂ H ₅	2

以下空白

例示構造化合物群〔Ⅶ〕:

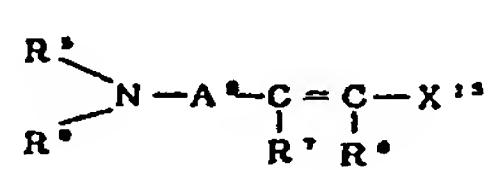
		
化合物No	X''	l
Ⅶ-1	—	0
Ⅶ-2	Cl	2
Ⅶ-3	Br	2
Ⅶ-4	"	3
Ⅶ-5	"	4
Ⅶ-6	I	4
Ⅶ-7	NO ₂	3
Ⅶ-8	CN	4
Ⅶ-9	COCH ₃	4

次に本発明で使用可能なCTMとしては、特に

制限はないが、例えばオキサゾール誘導体、オキサジアゾール誘導体、チアゾール誘導体、チアジアゾール誘導体、トリアゾール誘導体、イミダゾール誘導体、イミダゾロン誘導体、イミダゾリジン誘導体、ビスイミダゾリジン誘導体、スチリル化合物、ヒドラゾン化合物、ピラゾリン誘導体、オキサゾロン誘導体、ベンゾチアゾール誘導体、ベンズイミダゾール誘導体、キナゾリン誘導体、ベンゾフラン誘導体、アクリジン誘導体、フェナジン誘導体、アミノスチルベン誘導体、ポリ-β-ビニルカルバゾール、ポリ-1-ビニルピレン、ポリ-9-ビニルアントラセン等であってよい。

しかしながら光照射時発生するホールの支持体側への輸送能力が優れている外、前記CTMとの組合せに好適なものが好ましく用いられ、かかるCTMとしては、例えば下記例示構造化合物群〔Ⅸ〕又は〔Ⅹ〕で示されるスチル化合物が使用される。該例示構造化合物群中の個々の具体的化合物の数を併せ掲げるが、その全貌については特願昭61-195881号が参照される。

例示構造化合物群〔Ⅸ〕:

						
化合物No	-R''	-R''	-R'	-R''	-A-	-X''
Ⅸ-1			-H			
Ⅸ-2		"	"	"	"	
Ⅸ-3		"	"	"	"	
Ⅸ-4	-CH ₃	-CH ₃	"	-H	"	
Ⅸ-5	-C ₂ H ₅	-C ₂ H ₅	"	"	"	"
Ⅸ-6	"	"	"	"	"	
Ⅸ-7	"	"	"	"	"	
Ⅸ-8			"	"	"	

化合物No	-R ⁹	-R ⁸	-R ⁷	-R ⁶	-A ⁵ -	-X ^{1*}
IX-75			-H	-H		
IX-80			-H	-CH ₃	"	
IX-81			"	"	"	

例示構造化合物群〔X〕

$\text{R}^9 \text{---} \text{C}_6\text{H}_3 \text{---} \text{N}(\text{R}^{10}) \text{---} \text{CH}=\text{CH} \text{---} \text{X}^{1*}$			
化合物No	-R ⁹	-R ¹⁰	-X ^{1*}
X-1	-H		
X-2	"	"	
X-3	"	"	
X-4	"	"	

例示構造化合物群〔XII〕

$\text{R}^{13} \text{---} \text{C}_6\text{H}_3 \text{---} \text{N}(\text{R}^{10}) \text{---} \text{CH}=\text{N} \text{---} \text{N}(\text{R}^{17}) \text{---} \text{C}_6\text{H}_5$			
化合物No	-R ¹³	-R ¹⁰	-R ¹⁷
XII-1	-H	-CH ₃	-CH ₃
XII-2	"	"	-C ₂ H ₅
XII-3	"	"	
XII-4	"	"	
XII-5	"	-C ₂ H ₅	-CH ₃
XII-6	"	"	-C ₂ H ₅
XII-7	"	"	
XII-8	"	"	
XII-9	"	-CH ₂ CH ₂ OH	-CH ₃
XII-10	"	"	-C ₂ H ₅
XII-11	"	"	
XII-12	-Cl	"	"

化合物No	-R ⁹	-R ¹⁰	-X ^{1*}
X-32	-OCH ₃		
X-33	"	"	

また、CTMとして下記例示構造化合物群〔XI〕～〔XV〕で示されるヒドラゾン化合物も使用可能である。尚個々の具体的化合物の全容については特願昭61-195881号が参照される。

例示構造化合物群〔XI〕:

$\text{R}^{11} \text{---} \text{C}_6\text{H}_3 \text{---} \text{N}(\text{R}^{12}) \text{---} \text{CH}=\text{N} \text{---} \text{A}^{12} \text{---} \text{N}(\text{R}^{13}) \text{---} \text{R}^{14}$					
化合物No	-R ¹¹	-R ¹²	-R ¹³	-R ¹⁴	-A ¹² -
XI-1	-H	-H			
XI-2	"	"			"
XI-3	"	"	"		"

例示構造化合物群〔XIII〕:

$\text{R}^{15} \text{---} \text{N}(\text{R}^{16}) \text{---} \text{C}_6\text{H}_3 \text{---} \text{CH}=\text{N} \text{---} \text{N}(\text{R}^{17}) \text{---} \text{R}^{18}$					
化合物No	-R ¹⁵	-R ¹⁶	-R ¹⁷	-R ¹⁸	-R ¹⁹
XIII-1	-C ₂ H ₅	-C ₂ H ₅	-H		
XIII-2	"	"	"		"
XIII-3	"	"	"	"	
XIII-4	"	"	"		
XIII-5	"	"	"	"	
XIII-6	-C ₂ H ₅	-C ₂ H ₅	"		
XIII-7	-C ₂ H ₅	-C ₂ H ₅	"		"
XIII-8			"		"

化合物No	-R ¹⁰	-R ¹¹	-R ¹²	-R ¹³	-R ¹⁴
X III-19	-C ₆ H ₅	-CH ₂ CH ₂ Cl	-H		
X III-20	"	-C ₆ H ₅	"		-CH ₂
X III-21	"	"	"	"	-C ₆ H ₅
X III-22	-C ₆ H ₅	-C ₆ H ₅	"		

例示構造化合物群(XIV):

化合物No	-R¹⁰	-R¹¹	-R¹²	-R¹³	-R¹⁴	-X¹⁵
XIV-1	-H	-H	-H	-H	-H	
XIV-2	"	"	"	"	"	
XIV-3	"	"	"	"	"	

例示構造化合物群(XV):

$ \begin{array}{c} \text{X}^{10}-\text{C}-\text{CH} \\ \quad \\ \text{H} \quad \text{R}^{22} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{C} \\ \quad \\ \text{R}^{23} \quad \text{N} \quad \text{C}=\text{CH}_2 \\ \\ \text{R}^{24} \end{array} \begin{array}{c} \\$						
---	--	--	--	--	--	--

例示構造化合物群(XV):

化合物No	-R ¹⁰	-R ¹¹	-R ¹²	-R ¹³	-X ¹⁰
X V-1	-H	-H	-H	-H	
X V-2	"	"	"	"	
X V-3	"	"	-CH ₂	-H	
X V-4	"	"	-H	"	"
X V-5	"	"	"	"	
X V-6	"	-OCH ₃	"	"	"
X V-7	"	-H	"	"	
X V-8	"	"	"	"	

また、CTMとして下記例示構造化合物群(XVII)

で示されるアミン誘導体も使用可能である。

尚詳しくは特願昭61-195881号が参照される。

例示構造化合物群(XVII):

化合物No	-R ¹⁰	-X ¹⁰
X VII-1	-H	
X VII-2	"	
X VII-3	-Br	
X VII-4	-H	
X VII-5	"	
X VII-6	"	
X VII-7	"	

次に本発明のOCLに用いられてよいバインダは、体積抵抗 $10^8 \Omega \text{cm}$ 以上、好ましくは $10^{10} \Omega \text{cm}$ 以上、より好ましくは $10^{12} \Omega \text{cm}$ 以上の透明樹脂が用いられる。又前記バインダは光又は熱により硬化する樹脂を少なくとも50重量%以上含有するものとされる。

かかる光又は熱により硬化する樹脂としては、例えば熱硬化性アクリル樹脂、シリコン樹脂、エポキシ樹脂、ウレタン樹脂、尿素樹脂、フェノール樹脂、ポリエステル樹脂、アルキッド樹脂、メラミン樹脂、光硬化性の桂皮酸樹脂等又はこれらの共重合もしくは共縮合樹脂があり、その外電子写真材料に供される光又は熱硬化性樹脂の全てが利用される。又前記OCL中には加工性及び物性の改良(亀裂防止、柔軟性付与等)を目的として必要により熱可塑性樹脂を50重量%未満含有せしめることができる。かかる熱可塑性樹脂としては、例えばポリプロピレン、アクリル樹脂、メタクリル樹脂、塩化ビニル樹脂、酢酸ビニル樹脂、エポキシ樹脂、ブチラール樹脂、ポリカーボネート樹

例えば無水こはく酸、無水マレイン酸、ジブロム無水マレイン酸、無水フタル酸、テトラクロル無水フタル酸、テトラブロム無水フタル酸、3-ニトロ無水フタル酸、4-ニトロ無水フタル酸、無水ピロメリット酸、無水メリット酸、テトラシアノエチレン、テトラシアノキノジメタン、o-ジニトロベンゼン、m-ジニトロベンゼン、1,3,5-トリニトロベンゼン、パラニトロベンゾニトリル、ピクリルクロライド、キノンクロルイミド、クロラニル、ブルマニル、2-メチルナフトキノン、ジクロロジシアノバラベンゾキノン、アントラキノン、ジニトロアントラキノン、トリニトロフルオレノン、9-フルオレニリデン〔ジシアノメチレンマロノジニトリル〕、ポリニトロ-9-フルオレニリデン〔ジシアノメチレンマロノジニトリル〕、ピクリン酸、フタル酸等が挙げられる。

本発明において感光体層に使用可能なバインダ樹脂としては、例えばポリエチレン、ポリプロピレン、アクリル樹脂、メタクリル樹脂、塩化ビニル樹脂、酢酸ビニル樹脂、エポキシ樹脂、ポリウ

レタン樹脂、シリコン樹脂、又はこれらの共重合樹脂、例えば塩化ビニル-酢酸ビニル共重合体樹脂、塩化ビニル-酢酸ビニル-無水マレイン酸共重合体樹脂、ポリ-9-ビニルカルバゾール等の高分子有機半導体、その他電子写真材料に供される熱可塑性樹脂の全てが利用される。

また前記OCLは、電子受容性物質を含有してもよく、その他、必要によりCGMを保護する目的でオゾン酸化防止剤等を含有してもよく、前記バインダと共に溶剤に溶解され、例えばディップ塗布、スプレー塗布、ブレード塗布、ロール塗布等により塗布・乾燥されて $2 \mu\text{m}$ 以下、好ましくは $1 \mu\text{m}$ 以下の層厚に形成される。

本発明の感光体層の層構成は前記のように積層構成と単層構成とがあるが、CTL、CGLまたはOCLには感度の向上、残留電位ないし反復使用時の疲労低減等を目的として、1種または2種以上の電子受容性物質を含有せしめることができる。

本発明に使用可能な電子受容性物質としては、

レタン樹脂、フェノール樹脂、ポリエステル樹脂、アルキッド樹脂、ポリカーボネート樹脂、シリコン樹脂、メラミン樹脂等の付加重合型樹脂、重付加型樹脂、重縮合型樹脂、並びにこれらの樹脂の繰返し単位のうちの2つ以上を含む共重合体樹脂、例えば塩化ビニル-酢酸ビニル共重合体樹脂、塩化ビニル-酢酸ビニル-無水マレイン酸共重合体樹脂等の絶縁性樹脂の他、ポリ-9-ビニルカルバゾール等の高分子有機半導体が挙げられる。

次に前記感光体層を支持する導電性支持体としては、アルミニウム、ニッケルなどの金属板、金属ドラム又は金属箔、アルミニウム、酸化錫、酸化インジウムなどを蒸着したプラスチックフィルムあるいは導電性物質を塗布した紙、プラスチックなどのフィルム又はドラムを使用することができる。

CTLは既述のCTMを適当な溶媒に単独もしくは適当なバインダ樹脂と共に溶解もしくは分散せしめたものを塗布して乾燥させる方法により設ける。

C T Lの形成に用いられる溶媒としては、例えば、N,N-ジメチルホルムアミド、ベンゼン、トルエン、キシレン、モノクロルベンゼン、1,2-ジクロロエタン、ジクロロメタン、1,1,2-トリクロロエタン、テトラヒドロフラン、メチルエチルケトン、酢酸エチル、酢酸ブチル等を挙げることができる。

本発明に係る感光体層をC T LとC G Lの複層構成で形成する場合は、C T Lの膜厚は、好ましくは5~50 μ m、特に好ましくは5~30 μ mである。

C T L中のバインダ樹脂100重量部当りC T Mが20~200重量部、好ましくは30~150重量部とされる。

C T Mの含有割合がこれより少ないと光感度が悪く、残留電位が高くなり易く、これより多いと溶媒溶解性が悪くなる。

C G Lは、既述のC G MとC T Mを別々に、あるいは一緒に適当な溶剤に単独もしくは適当なバインダ樹脂と共に溶解もしくは分散せしめたものを塗布、乾燥してC T Lの場合と同様に形成することができる。

C G L中のバインダ樹脂100重量部当りC G Mが20~200重量部、好ましくは25~100重量部とされ、C T Mが20~200重量部、好ましくは30~150重量部とされる。

C G Mがこれより少ないと光感度が低く、残留電位の増加を招き、又これより多いと暗減衰が増大し、かつ受容電位が低下する。

以上のようにして形成されるC G Lの膜厚は、好ましくは1~10 μ m、特に好ましくは2~7 μ mである。

積層構成の場合、C G LとC T Lの膜厚比は1:(1~30)であるのが好ましい。

次に本発明の感光体を単層で構成する場合、C G Mがバインダ樹脂に含有される割合は、バインダ樹脂100重量部に対して20~200重量部、好ましくは25~100重量部とされる。

C G Mの含有割合がこれより少ないと光感度が低く、残留電位の増加を招き、又これより多いと暗減衰及び受容電位が低下する。

次にC T Mがバインダ樹脂に対して含有される

上記C G Mを分散せしめてC G Lを形成する場合、当該C G Mは2 μ m以下、好ましくは1 μ m以下の平均粒径の粉粒体とされるのが好ましい。即ち、粒径があまり大きいと層中への分散が悪くなると共に、粒子が表面に一部突出して表面の平滑性が悪くなり、場合によっては粒子の突出部分で放電が生じたり或いはそこにトナー粒子が付着してトナーフィルミング現象が生じ易い。

ただし、上記粒径があまり小さいと却って凝集し易く、層の抵抗が上昇したり、結晶欠陥が増えて感度及び繰返し特性が低下したり、或いは微細化する上で限界があるから、平均粒径の下限を0.01 μ mとするのが望ましい。

C G Lは、次の如き方法によって設けることができる。即ち、記述のC G Mをボールミル、ホモミキサ等によって分散媒中で微細粒子とし、バインダ樹脂およびC T Mを加えて混合分散して得られる分散液を塗布する方法である。この方法において超音波の作用下に粒子を分散させると、均一分散が可能である。

割合は、バインダ樹脂100重量部に対して20~200重量部、好ましくは30~150重量部とされる。

C T Mの含有割合がこれより少ないと光感度が悪く残留電位が高くなり易く、又これより多いと溶媒溶解性が悪くなる。

前記単層構成の感光体層中のC G Mに対するC T Mの量比は重量比で1:3~1:2とするのが好ましい。

また単層構成の感光体層の膜厚は7~50 μ m、更に好ましくは10~30 μ mである。

また、前記中間層は接合層又はバリヤ層等として機能するもので、上記バインダ樹脂の外に、例えばポリビニルアルコール、エチルセルロース、カルボキシメチルセルロース、塩化ビニル-酢酸ビニル共重合体、塩化ビニル-酢酸ビニル-無水マレイン酸共重合体、カゼイン、 γ -アルコキシメチル化ナイロン、澱粉等が用いられる。

次に本発明の正帯電感光体を用いる像形成プロセスを第4図を用いて説明する。

第4図は静電潜像につづいてトナー像を担持す

る本発明の感光体ドラムを取囲む、本発明の像形成プロセスに関与する諸機能部材の配置の1例を示す。

本発明の正帯電感光体20は、導電性支持体によりアースされており、正に整流されて正電荷を与えるコロナ放電極等の帯電器21(例えばスコトロロン等)によって、予め正帯電され時計方向(図に於てAの方向)に回転する。

また原稿載置台上の原稿からの反射光Eは、ミラー、レンズ等からなる光学系を経て感光体20(ドラム)上へスリットSを介して入射される。

感光体ドラム20は予め帯電器21により電荷を与えられているので、前記光学系からの光入射に従って感光体ドラム20上には原稿に対応した静電潜像が順次形成され、回転する感光体ドラム20上の前記静電潜像は、現像器22によって可視のトナー像となる。

一方、転写紙は給紙装置より繰出されて、ガイド板により案内されて給紙ローラ32に到り、感光体ドラム20上の前記トナー像の先端と転写紙との

クリーニング装置28と帯電器21との間に配設され、蛍光灯等の光源等から成る。クリーニング装置28で表面のトナーを除去された感光体ドラム20は、この前露光装置27によるクリーニング露光によって、ドラム表面の残留電荷は除かれ電位はゼロになる。

第2の前露光装置28は、現像器22と転写極23、分離極24との間、第3の前露光装置29は分離極その他の分離部の後にあってクリーニング除電極25の上流をなす位置に配設され、蛍光灯等の光源等から成る。この第2及び第3の前露光装置による光照射、即ち転写前露光及び消去露光によって、感光体ドラム20の表面電荷が低減・均一化され、これによって転写・分離時の効率が向上し、更には感光体ドラム20上の残像のクリーニングを容易にする。

〔実施例〕

以下本発明を実施例により説明するが、これにより本発明の実施の態様が限定されるものではない。

先端が一致するようにタイミング信号に基づいて給紙される。

その後、転写極23の作用により感光体ドラム20上のトナー像は転写紙上に転写される。そして分離極24により、感光体ドラム20上から分離された転写紙は転写紙搬送手段35を経て定着装置へ送られ、熱定着ローラおよび圧着ローラによって熔融定着されたのち、排紙ローラにより排紙皿上へ排出される。

一方、転写工程終了後、前記感光体ドラム20は、ドラム上に残留するトナーのクリーニング装置28による除去を容易にするため、交流のコロナ放電を行なうクリーニング除電極25によって、ドラム表面が電氣的に中和される。次いで転写しきれずにドラム上に残ったトナーはブレード等のクリーニング装置26により掻き落される。

これによりドラムは次のコピーへの準備ができる。

以上が複写を行なう基本のプロセスであるが、画質を高めるため、複写機には前露光といわれる工程が用いられる。第1の前露光装置27は前記ク

実施例 1

アルミニウム箔をラミネートしたポリエステルフィルム及びアルミニウムドラムより成る導電性支持体上に、塩化ビニル-酢酸ビニル-無水マレイン酸共重合体(エスレックスMF-10、積水化学工業社製)よりなる厚さ0.1 μ mの中間層を形成した。

次いでポリカーボネート樹脂(バンライトL-1250、帝人化成社製)/CTM(IX-75)=100/75(重量比)を16.5重量%含有する1,2-ジクロルエタン溶液を中間層上にディップ塗布し、15 μ m厚のCTLを形成した。次に、CGMとして昇華した4,10-ジブロムアンスアンスロン(VI-3)/バンライトL-1250=1/2(重量比)が9重量%になるように1,2-ジクロルエタン中ボールミルで24時間粉碎し、更に24時間分散した液にCTM(IX-75)をバンライトL-1250に対して75重量%およびCTMに対して10重量%の例示化合物(3)を加えた。この溶液にモノクロルベンゼンを加えて1,2-ジクロルベンゼン/モノクロルベンゼン=7/3(体積

比)になるよう調製した分散液を前記CTL上にスプレー塗布し、乾燥して5 μ mのCGLを形成し、積層構成の感光体層を有する本発明の感光体試料1を得た。

比較例 (1)

実施例1において、例示化合物(3)を除いた以外は実施例1と全く同様にして比較の感光体試料(1)を得た。

実施例 2

実施例1において、例示化合物(3)に代えて例示化合物(1)を用いた以外は全く同様にして感光体試料2を得た。

実施例 3

実施例1の例示化合物(3)を除いた感光体層(比較例1の感光体に同じ)上に、熱硬化性アクリル-メラミン-エポキシ(1:1:1)樹脂1.55重量部および例示化合物(3)0.155重量部をモノクロルベンゼン/1,1,2-トリクロルエタン混合溶媒に溶解させた塗布液をスプレー塗布し、乾燥して1 μ m厚のOCLを有する感光体試料3を得た。

次いでCGM(N-7)0.2gをペイントコンディショナ(Paint Conditioner、Red Devil社製)で30分粉砕し、これにポリカーボネート樹脂(バンライトL-1250、前出)を1,2-ジクロルエタン/1,1,2-トリクロルエタン混合溶媒に0.5重量%となるよう溶解させた溶液を8.2g加えて3分間分散し、次いでこれにポリカーボネート樹脂、CTM(X-75)および例示化合物(3)をそれぞれ3.3重量%、2.6重量%および0.26重量%となるよう1,2-ジクロルエタン/1,1,2-トリクロルエタン混合溶媒に溶解して得られる溶液19.1gを加えてさらに30分間分散した。かくして得られた分散液を前記CTL上にスプレー塗布し、かつ乾燥して5 μ m厚のCGLを形成し、積層構成の感光体層を有する感光体試料5を得た。

比較例 (2)

実施例5において例示化合物(3)を除いた以外は実施例5と全く同様にして比較の感光体試料(2)を得た。

実施例 6

実施例 4

実施例1の例示化合物(3)を除いた感光体層上に、シリコンハードコート用プライマPH91(東芝シリコン社製)を0.1 μ mとなるようスプレー塗布し、更にその上にシリコンハードコートトスガード510(東芝シリコン社製)及び例示化合物(3)を樹脂100重量部に対して10重量部となるよう添加した溶液をスプレー塗布し、乾燥して1 μ m厚のOCLを形成し感光体試料4を得た。

実施例 5

アルミニウム箔をラミネートしたポリエステルフィルム、及びアルミニウムドラムより成る導電性支持体上に、塩化ビニル-酢酸ビニル-無水マレイン酸共重合体(エスレックMF-10、前出)よりなる厚さ約0.1 μ mの中間層を形成した。

次いでCTL用塗布液としてブチラール樹脂(エスレックBX-1、積水化学社製)8重量%とCTM(X-75)6重量%をメチルエチルケトンに溶解して得られる塗布液を前記中間層上に塗布・乾燥して10 μ m厚のCTLを形成した。

実施例5において、例示化合物(3)に代えて例示化合物(1)を用いた以外は全く同様にして感光体試料6を得た。

実施例 7

実施例5の例示化合物(3)を除いた感光体層(比較例2の感光体に同じ)上に、実施例3と同様の例示化合物(3)を含有する保護層を設置し、感光体試料7を得た。

実施例 8

実施例5の例示化合物(3)を除いた感光体層上に、実施例4と同様の例示化合物(3)を含有する保護層を設置し、感光体試料8を得た。

前記実施例試料1~8及び比較例試料(1)、(2)についてUV耐性について、帯電性に対する2万回の実写テスト及びUV照射による感度変化の定量的測定を行った。

帯電性実写テストは、本発明の像形成プロセスを行うU-Bix 2812 MR(小西写真工業(株)製)の改造実験機に試料感光体ドラムを装着し、正帯電させ、前記感光体に対する像露光をはじめ

感度測定は静電試験機（川口電機製作所：SP-428型）によった。

これらの結果を第1表に示す。

第1表

感光体 試料No.	CGM	CTM	例示 化合物	+V _a	+V _s	S ₀	S ₁	R _s (%)
1	VI-3	IX-75	(3)	800	607	5.4	5.8	93
(1)	"	"	—	600	694	5.4	10.0	54
2	"	"	(1)	600	808	5.5	5.9	93
3	"	"	(2)	800	610	6.4	6.9	93
4	"	"	(2)	600	809	6.0	6.4	94
5	IV-7	"	(2)	800	808	4.5	4.9	92
(2)	"	"	—	600	690	4.4	8.0	55
6	"	"	(1)	600	610	4.8	5.0	92
7	"	"	(3)	800	610	5.4	5.9	92
8	"	"	(3)	600	610	5.0	5.4	93

注：括弧を付した番号は比較試料

とする各工程及び定着からなる単位サイクルを2万回繰返し、実写テスト初期の正帯電電位を+V₀、2万回終了後の正帯電電位を+V₁とする。

またUV照射による感度変化は、既知強度の紫外線を試料フィルムを遮断した感光体シートに照射し、その照射前後に於て、+800Vに帯電させた該感光体の電位を+100Vまで露す露光量E₁₀₀を用いて求めた。

感光体の感度SはE₁₀₀ ∝ 1/Sの関係として定義され、E₁₀₀が小さいほど感度Sは大きく硬調な画像がえられる。

UV照射前後の感度を夫々S₀、S₁とすれば、その逆数比R_s:(1/S₁)/(1/S₀)=S₀/S₁はUV耐性を表し、R_sが大きいほどUV耐性があることになる。

UV照射は理化学用水銀ランプSHL-100UV-2（（株）東芝製）を用い試料フィルムを断裁した感光体シートを30cmの距離に置き他の電磁波を遮断し、UV強度1500cd/cm²で100分間照射を行い、

比較用感光体は紫外線劣化が著しく電子写真特性も良くないことが判る。

4. 図面の簡単な説明

第1図ないし第3図は本発明の正帯電感光体の断面図である。

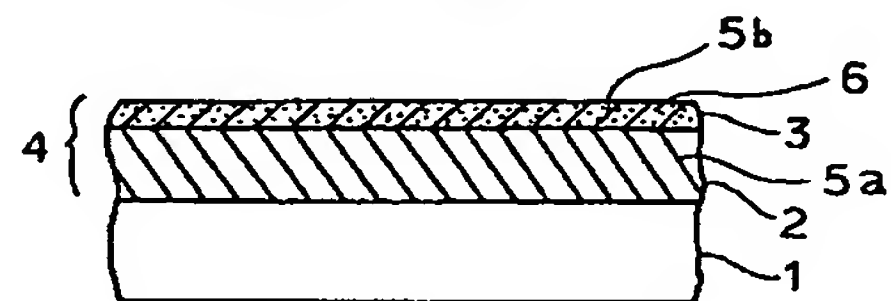
第4図は像形成プロセスの説明図である。

- 1…支持体
- 2…電荷輸送層(CTL)
- 3…電荷発生層(CGL)
- 4…感光体層
- 5…電荷輸送物質(CTM)
- 6…電荷発生物質(CGM)
- 7…保護層(OCCL)
- 20…感光体
- 21…帯電器
- 22…現像器
- 26…クリーニング装置
- 27,28及び29…前露光装置

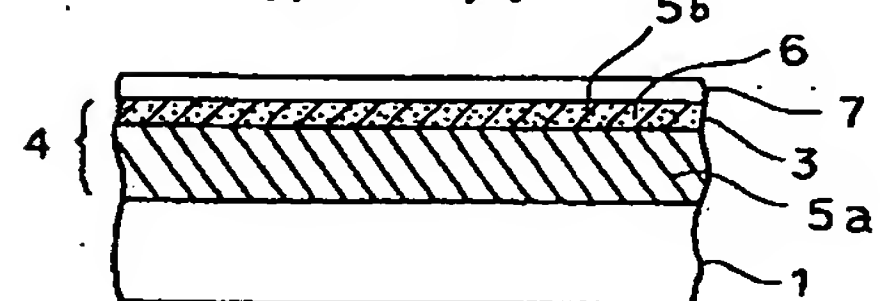
出願人 小西六写真工業株式会社

第1表から本発明の感光体はいずれも紫外線耐性および電子写真特性共にすぐれているのに対し、

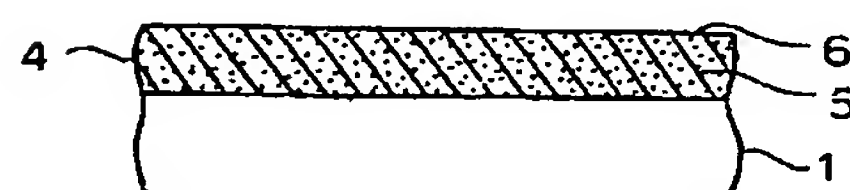
第1図



第2図



第3図



第 4 図

